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DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.[1]

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This research was undertaken in compliance with the instructions of a letter from the President of the National Board of Health, written on behalf of the Executive Committee of the Board, and dated Washington, December 29, 1880.

A full report on the objects, in detail, of the investigation, on the methods employed, and the results obtained, has been prepared and placed in the hands of the Board. Pending its publication *in extenso*, the Executive Committee has thought proper to direct that an abstract, covering the principal conclusions reached, shall be published. The following pages present such an abstract.

It was intended to examine carefully the chief processes in use for chemically determining the organic matter, or its constituents, in drinking-water, to test the absolute and relative accuracy of the results these processes are capable of yielding, and as far as possible to ascertain the nature and scope of the practical conclusions available for sanitary purposes which may thence be secured.

Three chemists took charge severally of the so-called "combustion process" of Frankland and Armstrong, the "albuminoid-

[1] Preliminary report on the results of an investigation, made by direction of the National Board of Health, as to the chemical methods in use for the determination of organic matter in potable waters.

ammonia process" of Wanklyn, Chapman, and Smith, and the "permanganate process," originally suggested by Forchhammer, in the form advocated and minutely described by Tidy. These gentlemen, Mr. W. A. Noyes, Dr. Charles Smart, U. S. A., and Dr. J. A. Tanner, U. S. N., worked independently, the first in the laboratory of the Johns Hopkins University, at Baltimore, by permission of its authorities, the second at the office of the National Board of Health, in Washington, and the third in the laboratory of the University of Virginia. Arrangements were made to have the samples of water for examination collected, and distributed to these three points by myself, so that there should be identity of material submitted to each analyst, and all three analysts should examine their several samples on the same day. Prof. H. Newell Martin, of the Johns Hopkins University, kindly undertook a simultaneous microscropic examination of the waters placed in the hands of the chemists, as also a series of pathological observations on the effect of injecting the waters, concentrated by evaporation at very low temperature, beneath the skin of rabbits, whose temperature and general condition were compared with those of like animals not so treated.

A large amount of preliminary and special work was done in the early part of 1881, the former chiefly with a view to making the analysts thoroughly familiar with the processes to be tested before coming to the actual tests themselves, the latter on various modifications of the processes in detail, and incidental points in connection with them of sanitary interest. From this work a number of results of considerable interest have been obtained, but their publication will have to be made in their place in the general report.

For the main series of test analyses, the following classes of waters were obtained or prepared:

Class I.—Natural waters, believed from actual use to be of good, wholesome character, including the regular water supply of some of the principal cities of the United States.

Class II.—Natural waters which there seems to be fair ground for believing have actually caused disease on the part of those drinking them. A request for information as to such waters, and for samples of them, was published for several months in the *National Board of Health Bulletin*, and was extensively copied into newspapers and professional journals, and a copious correspondence with physicians and others in various parts of the country

was employed to secure such samples, and to sift the evidence as to the supposed connection of the use of each water with the production of disease.

CLASS III.—Natural waters, of doubtful, but more or less suspected, character. In reference to these the medical evidence was insufficient to justify placing them in Class II.

CLASS IV.—Artificially prepared waters, made by adding to good, wholesome water, determinate amounts of various infusions of *vegetable* organic matter, of natural origin, and of such kinds chiefly as water for human consumption is liable to be brought in contact with.

CLASS V.—Artificially prepared waters, made as above, with various forms of *vegetable* refuse from manufacturing or industrial operations.

CLASS VI.—Artificially prepared waters, as above, made with *animal* (or partly animal) organic matter of natural origin, especially such as are likely to occur in connection with the contamination of drinking water.

CLASS VII.—Artificially prepared waters, as above, made with *animal* refuse from manufacturing or industrial operations.

CLASS VIII.—Artificially prepared waters, as above, to which had been added morbid products from certain diseases in the human subject.

CLASS IX.—Solutions in distilled water, of carefully determined amounts of pure substances of definite chemical composition.

The results obtained from the examination of a large number of samples, representing the above classes of waters, are given in detail in a table in the general report. At present the conclusions reached in the discussion of these results can alone be given.

GENERAL DISCUSSION OF RESULTS.

Degree of accuracy of the three principal processes examined.—This may be looked at in two ways: first, as to the concordance of the results obtained by each process in duplicate or triplicate experiments on the same water; and, secondly, as to the agreement of the results obtained with the actual contents of a particular water when these are quantitatively known.

In the former of these aspects we have to do with such errors as are, practically speaking, fortuitous; in the latter we notice especially the indications of constant errors inherent in the methods used.

Extent of concordance of the results obtained by each process in multiplied experiments on the same water.—This has been tested by taking the mean of duplicate or triplicate determinations, noting the difference between this mean and each of the individual determinations on which it was based, and calculating this difference as percentage on the mean itself. The data for such calculation have been most numerous in the case of the combustion process, since it was considered necessary to make duplicate analyses all through the research, with a number of triplicates. It is the more important that this process should be thus examined, in view of the objection which has been often made to it, that it demands an unusual degree of skill and training on the part of the experimenters. In connection with the extensive work of the English Commission on the Pollution of Rivers, it is to be supposed that many duplicate analyses must have been made by this method, but there has appeared but little in print to show how far these were concordant. The results obtained in the course of the present research are summarized in tables XI, XII, and XIII.

TABLE XI.—*Extent of disagreement of results of multiplied analyses of same water by combustion process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For all waters in classes I to VIII, inclusive, save the few for which there was but one analysis, and those for which there was a known source of error vitiating one of the analyses :[1]			
Organic carbon	24.46[2]	0	4.24
Ditto, rejecting twelve cases in which the divergence was over 10 per cent. (ten of these cases involved very minute absolute quantities of carbon)	9.96	0	2.89
Organic nitrogen	40.00[3]	0	9.48
Ditto, rejecting thirteen cases in which the divergence was over 20 per cent. (ten of these cases involved very minute absolute quantities of nitrogen)	19.82	0	7.09

[1] Representing in all two hundred and sixty-two separate analyses for carbon and two hundred and forty-six for nitrogen. (Some analyses for the latter element were vitiated by uncertainty in the determination of free ammonia, and hence in the amount to be subtracted for this latter.)

[2] Actual difference was less than .3 milligram.

[3] Actual difference was only .04 milligram.

TABLE XI.—*Continued.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For the waters in Class IX (solutions of definite chemical substances in known amount)[1]:			
Organic carbon	50.00[2]	.15	9.54
Ditto, rejecting six cases in which the divergence was over 10 per cent. (four of these cases involved very minute absolute quantities of carbon)	7.76	.15	2.81
Organic nitrogen	14.52[3]	0	5.05
Ditto, rejecting five cases in which the divergence was over 10 per cent. (but one of these cases involved a very minute quantity of nitrogen)	9.75	0	2.71
Average of both the above sets of experiments, giving them equal weight:			
Organic carbon (including all cases)	37.23	.07	6.89
Ditto (rejecting in all thirty-six extreme cases, as above)	8.86	.07	2.85
Organic nitrogen (including all cases)	27.26	0	7.26
Ditto (rejecting in all thirty-six extreme cases, as above)	14.78	0	4.90

[1] Representing in all forty-one separate analyses each for carbon and nitrogen. (One determination for each was without a duplicate, and hence had to be rejected from the data for this table.) [2] Actual difference was .035 milligram. [3] Actual difference was .47 milligram.

TABLE XII.—*Extent of disagreement of results of multiplied experiments on same water by albuminoid-ammonia process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For thirteen waters in Classes I to VIII, examined in triplicate:[1]			
Free ammonia	36.05	0	5.91
Ditto, rejecting two cases, involving very minute quantities of free NH_3	19.05	0	2.79
Albuminoid ammonia	8.51	0	2.69
For waters of Class IX (twenty-one in all—all examined in duplicate):[2]			
Free ammonia	5.53	0	1.67
Abuminoid ammonia	14.28	0	6.19
Ditto, rejecting four cases involving very minute quantities of alb. NH	12.79	0	4.56
Average of both the above sets of experiments, giving them equal weight:			
Free ammonia (including all cases)	20.79	0	3.79
Ditto (rejecting two extreme cases, as above)	12.29	0	2.23
Albuminoid ammonia (including all cases)	11.39	0	4.44
Ditto (rejecting four extreme cases, as above)	10.65	0	3.62

[1] Representing thirty-nine separate determinations.

[2] Representing forty-two separate determinations; of course purely negative results are not included in the data for this table.

TABLE XIII.—*Extent of disagreement of results of multiplied experiments on same water by permanganate process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For twelve waters in Classes I to VIII, examined in duplicate:[1]			
Oxygen consumed in one hour[2]	4.70	0	1.09
Oxygen consumed in three hours[3]	4.35	0	.56
For waters of Class IX (twenty-one in all—all examined in duplicate):[4]			
Oxygen consumed in one hour[5]	8.33	0	.62
Oxygen consumed in three hours[6]	6.66	0	1.10
Average of both the above sets of experiments, giving them equal weight:			
Oxygen consumed in one hour	6.51	0	.85
Oxygen consumed in three hours	5.50	0	.83

[1] Representing twenty-four separate determinations.

[2] Including five cases in which divergence was over 1 per cent. (in all these but very little oxygen was consumed).

[3] Including two cases in which divergence was over 1 per cent. (in these very little oxygen was consumed).

[4] Representing forty-two separate determinations. Of course those are not included in the data for this table which showed no oxygen, or but a mere trace, consumed.

[5] Including one case in which divergence was over 1 per cent. (very little oxygen consumed).

[6] Including three cases in which divergence was over 1 per cent. (very little oxygen consumed).

Of the figures given in the last column of Table XI, those which probably represent with most fairness the average departure from the mean of an individual determination by the combustion process[1] are:

For organic carbon . . 2.89 per cent.
For organic nitrogen . . 7.09 "

This goes in part to support the opinion of Tidy[2] that the results of the combustion process are less to be relied on for nitrogen than for carbon.

The results shown for the waters of Class IX are less deserving of attention in this particular respect, since there were but seven different organic substances included, and these specially selected. The reversal of position of the carbon and nitrogen results in

[1] See Mills' conclusions from a much more limited basis of induction furnished by a few of Frankland's analyses—Jour. Chem. Soc. (Lond.), February, 1878, 58 *et seq.*

[2] Jour. Chem. Soc. (Lond.), January, 1879, 56.

this class as compared with the preceding, is partly due to great and variable loss by evaporation of the volatile organic acids, and by dissociation of the salts of amines, &c.

From the last column of Table XII, the figures which probably may most fairly be taken to represent the average divergence from the mean of a single determination by the albuminoid-ammonia process are:

For free ammonia . .	2.23 per cent.
For albuminoid ammonia . .	3.62 "

We should naturally expect to find greater irregularity in the evolution of the so-called albuminoid-ammonia, though the conditions of chemical action be made as nearly as possible the same.

As regards the averages in the last column of Table XIII, the consumption of oxygen by the waters in Class IX having been for the most part very small, it seems probable that, for practical purposes, the first figures may best be taken, viz:

For oxygen consumed in one hour .	1.09 per cent.
For oxygen consumed in three hours .	.56 "

showing somewhat greater irregularity in the early stage of the action than later.

It will be seen that on the whole the most closely concordant results were furnished by the permanganate process, and the least so by the combustion process, the albuminoid-ammonia process holding the intermediate position.

Extent of agreement of the results obtained by the different processes with the quantities of organic constituents known to be actually present.—The detailed evidence under this head is given in columns 19 to 25, inclusive, of the last sheet of Table X, in which the results actually obtained on examination of the waters in Class IX (solutions of known amounts of certain organic substances of definite chemical composition) are compared with the amounts of the organic elements really present and the calculated amounts of oxygen required for their complete oxidation.[1] The following summary (in Table XIV) presents the conclusions reached within the limits of these experiments.

[1] In this calculation hydrogen has been taken as converted into water, carbon into carbon dioxide, and nitrogen as evolved in uncombined form; of course no one would expect any such ultimate results of oxidation from the action of the permanganate as practically applied. Frankland, in a similar calculation (Jour. Chem. Soc. (Lond.), March, 1868, 83), seems to have taken the nitrogen as oxidized to nitric acid.

TABLE XIV.—*Extent of agreement of results obtained by the different processes with the known chemical character of the waters in Class* IX.

	Amounts obtained, as percentage upon amounts calculated.		
	Greatest.	Least.	Average.
Combustion process:			
Organic carbon	85.	1.	53.
Organic nitrogen (including that of ammonia)	180.	47.	118.
Albuminoid-ammonia process:			
	Greatest.	Least.	Average.
Nitrogen of free NH_3[1]	94.	0.	(28.)[2]
Nitrogen of alb. NH_3[1]	84.	0.	(24.)[2]
	95.	0	53.
Permanganate process:			
Oxygen consumed in one hour	13.	0	3.
Oxygen consumed in three hours	16.	0	4.

(In this table, as in the last sheet of Table X, a considerable fraction of 1 per cent. is represented by 1—; an insignificant fraction is considered = 0.)

The figures of this table strikingly indicate certain important defects of the several processes, although they must be looked at in a broad, general way, remembering the small number of organic substances treated, and their special characters.

As regards the combustion process, we find loss of carbon, in all cases considerable, and in some cases very great; with a strong tendency on the whole to excess of nitrogen, which in some cases is very great. It is of course easy to see how, in large measure at least, these errors were caused for some of the samples. Thus, doubtless, free butyric and valerianic acids were formed from their salts, and volatilized with the water during its evaporation; the salts of the amines probably suffered partial dissociation, with volatilization of the bases; and urea was lost after conversion into ammonium carbonate. It may be objected that such substances as these ought not to have been selected. But it is to be remembered that every one of them occurs among the products of putrefactive decay of albuminoid or other organic matter, and hence may fairly be looked for among the constituents of organically polluted water.[3]

[1] Both calculated as percentage on *total* nitrogen present.

[2] These two averages have no real significance.

[3] Fresenius and Scherer have found butyric and propionic acids in the mineral water of Brückenau and Weilbach. Zeitschrift für anal. Chem. **20**, 3, 325.

The occurrence of loss of organic constituents during the evaporation of water for the combustion process has often been suspected by the critics of that process,[1] and often, though sometimes cautiously, denied by its advocates. Thus Mills has said:[2] "Substantially satisfactory evidence has been adduced that there is no material loss during the evaporation." The experiments now reported prove exactly the reverse of this, and furnish for the first time, as far as I know, direct evidence of the fact that, for some organic substances at least, and those of a kind liable to occur among the products of putrefaction, there *is* material, nay, very great loss.

As regards the frequently presented excess of nitrogen, I am strongly inclined to believe it in part at least due to absorption, during the evaporation of the acidified water, of ammonia *from the atmosphere surrounding the gas flame* and water-bath. Due care was taken as to the general condition of the atmosphere of the room, and it hardly seems possible to account for the error from this source.[3] But any one who has noticed the considerable deposit of ammonium sulphate formed on platinum vessels over an ordinary laboratory lamp or on bells suspended over household gaslights, will readily admit that here is a manifest source of danger. The extent to which ammonia is removed from coal gas at different works, and in the same works at different times, varies no doubt a good deal, but all American gas which I have examined readily shows its presence. With the gas in use at the University of Virginia and the neighboring town of Charlottesville, I find that when not ignited it will in five seconds produce a distinct yellow stain on a drop of the Nessler reagent upon white filtering paper, and, although no doubt much ammonia undergoes combustion when the coal gas itself is burning, a platinum capsule of three inches in diameter, containing water to keep it cool, will, if held over the flame of a Bunsen burner for half a minute, and the outside surface then washed off into a test-glass, yield a liquid which distinctly gives the Nessler reaction for ammonia. During the many hours of the evaporation of a water sample there must occur

[1] Wanklyn asserts in the most positive way the occurrence of loss, but gives no experimental evidence in support of his assertion. (Water Analysis, London, 1879, 190.)

[2] Jour. Chem. Soc. (Lond.), February, 1878, 58.

[3] The most scrupulous pains, too, were taken to guard against leakage of air into the Sprengel vacuum and nitrogen from the cupric oxide, and errors from these sources could scarcely have failed to be detected. They were examined into over and over again.

in the atmosphere about the water-bath a quantity of nitrogen in the form of ammonia which may well be called very large in comparison with the amounts dealt with by the water analyst, and although contact of the contents of the glass dish with this atmosphere is largely cut off by the glass shade, such contact is not entirely prevented, as there is the notch in the rim of the water-bath for the passage of the feed-flask neck. The avidity with which such ammonia as may reach the acid water will be absorbed by it is obvious enough, even though some be afterwards lost by dissociation. The excess of nitrogen observed in the analyses of Class IX seems to be general; even in those cases in which a loss is recorded it will be noticed that this loss is always less than for the carbon of the same substance, and the result is most probably a mere balance between two errors in opposite directions, actual loss of organic nitrogen volatilized in some form during the evaporation of the water, very possibly to even a greater extent than for carbon, and on the other hand absorption of nitrogen as ammonia from the atmosphere.

In reference to the results obtained by the albuminoid-ammonia process, little more is presented than has already been fully discussed in an earlier part of the general report. The total loss of the amine bases by volatilization during the first distillation (with sodium carbonate) results practically, as these bases do not produce the ammonia color with the Nessler reagent, in their nitrogen escaping recognition under the head of either "free" or "albuminoid" ammonia. Here we have a proof that some, at least, of the nitrogenous products of putrefaction are not detected or determined by this process as usually conducted.[1] There is no discrepancy between the results as to these bases here noticed, and that recorded for a triethylamine salt in Table VII of the general report: in this last mentioned case the salt was in contact with alkaline permanganate from the commencement of the distillation.

The results in this Class IX by the permanganate process have mainly the same sort of interest. It has, of course, long been known that, in the words of Tidy,[2] "there are many substances (most of which are crystalline) that are altogether unacted upon, or very slowly acted upon, by the oxygen of permanganate"; but

[1] Wanklyn has excepted nitro-compounds and (erroneously) urea, but clearly implies that these are the only exceptions; that the nitro-compounds are without practical importance, and that urea is specially provided for. Water Analysis, London, 1879, 189.

[2] Jour. Chem. Soc. (Lond.), Jan. 1879, 78.

it has been distinctly claimed for this process[1] by the same chemist that "it undoubtedly furnishes us with exact information as to the relative quantities of putrescent and easily oxidizable matter, and of non-putrescent or less easily oxidizable matters, present in the water. The former (viz. the putrescent organic matters) it indicates quantitatively with great accuracy; the latter (viz. the non-putrescent matters) are scarcely capable of the same exact estimation as the former, for they are bodies for the most part of difficult oxidation." Now here we have some of the definite substances which are actually known to occur among the constituents of putrescent albuminoid matter, and it needs but a glance at the table to see how limited is their oxidation by the cold acid permanganate, and yet how considerable are the differences in behavior of these few substances selected mainly on the same general principle.

Of course it is not assumed that the figures in Table XIV really represent either the range of absolute error, or the average amount of absolute error, of the different processes as applied to the doubtless very various forms of organic matter liable to occur in natural waters; these figures do, however, illustrate the existence of sources of absolute error, and by examples taken from the very class of substances which it has been most commonly believed important to detect and determine in water analysis.

Effect on the results by the different processes of varying the extent of dilution of the same organic substances in water.—The evidence in regard to this point is graphically presented in Tables XV, XVI, and XVII.

(These tables will appear with the general report.)

In studying these tables, indications of definite effects on the results of the various processes arising from the degree of dilution of the liquids examined soon become apparent, but seem to be subject to much irregularity. Such irregularity, however, is much reduced by a careful consideration of all the circumstances affecting individual cases. Thus, some of the numerical results of analysis ought to be omitted from consideration as vitiated by known errors, as in the case of albuminoid ammonia determinations in obtaining which the whole of the alkaline permanganate was reduced, or an obviously considerable part of the ammonia was still coming off when the process had to be stopped. In other cases the value of

[1] *Loc. cit.* 80.

the results is rendered doubtful by the solution examined having been excessively dilute or excessively strong; the relatively greater analytical errors for the former, and for the latter the errors of measurement of very small quantities of the liquid itself, and greater uncertainty as to its uniformity when turbid, tend to make the figures obtained less trustworthy than when intermediate degrees of concentration were involved; Nos. 110 to 118 inclusive represent the former source of abnormal results, such waters as No. 100 the latter. Again, the three solutions containing each form of polluting material in different degrees of dilution were, as has been explained, necessarily examined on different days, and evidence of changes going on in the meantime are to be found in the relative amounts of free and albuminoid ammonia, the character of the dissolved gases, &c. (see for the latter Nos. 83, 84, 85); hence, the *order* in which the three solutions of each group were examined has to be taken into account. Further, the results of one of these tables have often to be considered in their bearing on those of the others, as, for instance, the free ammonia determinations as affecting the value of the figures for organic nitrogen. And, lastly, after having observed the general drift of the errors indicated, we can see in the varying balance of errors of opposite effect an explanation of many apparently exceptional figures.

The general results of such detailed study of individual cases agree with those obtained by a simple calculation of averages, omitting from the calculation such figures as on sound grounds of general principle are to be regarded as vitiated for the purpose of this discussion. In the following table the solutions of the seven pure chemicals (Nos. 141 to 161) have been left out on account of the abnormal relations of these (which have been separately discussed) to some of the processes. For the combustion process, two other substances, represented by the dilutions Nos. 101 to 103, and 122 to 124, are omitted, because in the former of these the figures for organic carbon are known to be of very little value, and those for organic nitrogen are entirely valueless in consequence of the uncertain determinations of free ammonia present in large qnantity (which had to be subtracted from the gross results of analysis), while in the latter the very large amount of the free ammonia correction makes the results doubtful. For the albuminoid ammonia process, those determinations of free ammonia originally marked by Dr. Smart as uncertain (by a ?), have been

omitted, and those determinations of albuminoid ammonia in making which the regular charge of alkaline permanganate was entirely reduced, requiring an additional charge to be afterwards added, or dilution to be resorted to. For the Kubel form of the permanganate process one or two cases have been omitted, in which the permanganate was entirely reduced, making the result valueless save as an approximation. Rejecting these obviously worthless data, the averages from all others are given in Table XVIII.

TABLE XVIII.

Average results obtained for different dilutions of same solution of organic matter.

	One-fifth per cent. strength.		One per cent. strength.	Five per cent. strength.	
	Calculated.	Obtained.	Assumed.	Calculated.	Obtained.
Combustion process:					
Organic carbon	20.	17.5	100.	500.	549.8
Organic nitrogen	20.	25.2	100.	500.	372.2
Albuminoid-ammonia process:					
Free ammonia	20.	39.9	100.	500.	445.3
Albuminoid ammonia	20.	27.2	100.	500.	257.9
Permanganate process:					
Tidy method—					
Oxygen consumed in one hour	20.	19.7	100.	500.	475.0
Oxygen consumed in three hours	20.	20.0	100.	500.	468.9
Kubel method—					
Oxygen consumed	20.	19.9	100.	500.	475.9

As regards the combustion process, we find distinct confirmation of the existence of the two forms of constant error which have been pointed out as affecting the evaporation.[1] The weaker the solution, or in other words, the larger the quantity of water to be evaporated for a given amount of organic matter, the less is the amount of organic carbon obtained, indicating relatively greater loss of this element. On the contrary, the weaker the solution or

[1]Compare the results observed by Mills (Jour. Chem. Soc. (Lond.), Feb. 1878, 60) in using evaporating dishes of different diameters. The larger dish gave a rather lower result for carbon, and higher for nitrogen.

the greater the quantity of water to be evaporated, the larger is the figure for organic nitrogen, indicating relatively greater gain of this element from the atmosphere, and probably in some cases less dissociation of ammoniacal salts, when the amount of free ammonia found is considerable. If the usual interpretation of Frankland's C : N ratio be applied, the curious and important result of these sources of error, affecting the two elements in opposite directions, follows, that the more dilute an organically polluted water is, the more animal-like in origin will its polluting material seem to be, while the stronger it is the greater will be the tendency to refer the contamination to a vegetable source; this distortion of the conclusions to be drawn from an examination by the combustion process is manifestly in the opposite direction to that commonly assumed to be safe.

In reference to the albuminoid ammonia process, the weaker the solutions are, the higher are the results obtained, both for free and albuminoid ammonia,[1] the influence common to both being probably that of imperfect condensation in the distillation, having a less effect as the quantity of ammonia is smaller. As for the albuminoid ammonia, the lower results obtained from the stronger solutions may be partly due to the smaller proportion borne by the fixed charge of alkaline permanganate to the quantity of organic matter to be acted on. The great irregularity in individual analyses is strongly indicative of a varying balance of errors from different sources. It will be observed that the discrepancy between the calculated figures and those of experiment is greatest for free ammonia in the case of the weakest dilution, while the reverse is true for albuminoid ammonia.

The results of the permanganate process are shown to be much less influenced by varying dilution within the limits involved in these experiments than those of the other processes. In the case of the solutions of greatest strength somewhat smaller figures are obtained for the oxygen consumed than calculation calls for.[2] This is probably due to the fact that for the weaker waters the ordinary fixed charge of permanganate added at the first leaves at

[1] This agrees with Dr. Smart's single experiment on Washington sewage in its original form and diluted. See "remarks" on No. 116 in Table X of general report.

[2] Some indications of a like result may be noticed in a few experiments of Tidy (Jour. Chem. Soc. (Lond.), January, 1879, 80, 81), though the variation in strength of his solutions was not so great, and he himself draws the conclusion that the consumption of oxygen was proportional to the strength.

the close of the process a relatively larger excess than is present when successive additions of the reagent have been made to a water strong enough to reduce the first charge completely.

We must not confound the effect of varying the amount of organic matter in relation to the permanganate by which it is to be oxidized with that of varying greatly, but to the same extent, the degree of dilution of both organic matter and permanganate at the same time. Dr. Tanner's experiments showed that under the latter head a solution of even potassium nitrite might be made so dilute that its action on a correspondingly small quantity of permanganate was rendered very slow.

It may, perhaps, be said in reference to all these experiments on varied dilutions of the same materials, that the several processes under examination are intended for use on water of approximately suitable character for drinking, not on comparatively strong solutions of organic matter, such as many of those I have employed, but the answer to this objection is, that these liquids were taken in order to *exaggerate*, and hence bring to light any defects inherent in the several processes, so far as such depend upon the simple condition of the amount of polluting material in proportion to that of pure water.

SPECIAL CONCLUSIONS AS TO THE COMBUSTION PROCESS.

These may be briefly stated as follows:

1. The combustion itself, carried out according to the directions of Frankland, is a process of great delicacy, and quite satisfactory in its details with proper precautions and in trained hands. There seems to be no advantage in employing any of the various modified ways of determining the gaseous products of combustion which have been proposed instead of gaseous volumetric analysis with the aid of the Sprengel vacuum.

2. The Frankland process is quite within the reach of the manipulative skill of any fairly-trained chemist, but it requires practice, and probably pretty constant practice. It cannot be taken up offhand and even tolerable results obtained at once. From the hands of a person without proper laboratory training, its results are utterly valueless. It is hence better adapted to regular use in the examination of many samples of water in a large public laboratory than to occasional use by a private individual in now and then examining a single water.

3. The defective point in the process is the failure of the evaporation to leave a residue representing the original organic matter of the water. This, which has been hitherto more or less suspected, has been established as a fact by the investigation now reported on. The process being conducted according to the directions of its authors, there are two constantly present errors, varying, but usually important in amount, namely, loss of carbon,[1] and gain of nitrogen from the atmosphere, the latter probably partly balanced by loss of that originally present in the water. These errors are relatively greatest when the quantity of organic matter in the water is small.

4. These errors, affecting unequally the carbon and nitrogen, are liable to alter the statement of C : N. ratio,[2] and hence to distort the sanitary conclusions usually drawn therefrom.

5. The result for organic nitrogen, as obtained by the combustion process, is also affected indirectly by the errors connected with the determination of the ammonia ("free ammonia"), as the nitrogen belonging to this has to be subtracted from the gross result. The existence of such errors, as from imperfect condensation of the ammonia, progressive decomposition of urea and other amides, &c., has been pointed out in previous pages of this report, and will be referred to in the conclusions as to the albuminoid-ammonia process.

6. There is a further indirectly operative cause of error as to the nitrogen, arising from the varying loss of ammonia by dissociation of its salts during the evaporation of the water. Frankland recognizes the necessity of a correction for this, which correction he makes depend upon the amount of ammoniacal salts present, but it is almost certain that the time occupied in the evaporation will also influence the extent of loss by dissociation. Error from this source will in most cases be very small, but may affect to a not unimportant extent the result for *organic* nitrogen.[3]

7. The combustion process involves special difficulties in the presence of nitrates, for which difficulties no completely satisfactory

[1] In connection with this a number of Dr. Smart's experiments are noteworthy, in which the distillate for free ammonia furnished evidence, by its haziness and greenish color, distinct from that which the Nessler reagent should have yielded, that volatile organic matter was present.

[2] In Prof. W. R. Nichols' Report on the Boston Water Supply (Fourth Annual Report of Boston Water Board, 1880), variations of the C : N ratio, extending from a given value to one three or three and a half times as great are observable for the Cochituate water within a few weeks, and still greater variations for the Mystic water.

[3] Examples are furnished by Frankland of analyses in which the ammonia correction is very large in comparison with the organic nitrogen.

remedy is as yet proved to have been found. M. W. Williams' mode of applying the copper-zinc couple for this purpose is deserving of more precise quantitative examination than it has yet received. The simultaneous presence in a polluted water of urea with nitrites and nitrates presents a case of peculiar difficulty involving several sources of error.

8. The formation of sulphuric acid during the evaporation of the water with sulphurous acid seems to be of more frequent occurrence than has hitherto been recognized. Mr. Noyes seems to think that to this source—small amounts of cupric sulphate being formed on mixture of the residue with cupric oxide—may perhaps be attributed the occasional presence, as noticed by Frankland, of traces of free oxygen among the gaseous products of combustion. This occurrence of sulphuric acid in the water residue, even in minute amount, is undoubtedly much to be deprecated, though its effect, at any rate on the carbon determinations, has not seemed to be as great as might have been expected.

9. The combustion process in its present form cannot be considered as "determining" the carbon and nitrogen of the organic matter in water in a sense to justify the claim of "absolute" value for its results which has been denied to those of all other methods. It is but a method of approximation, involving sundry errors, and in part a balance of errors.

10. There is, however, good ground for believing that in many, perhaps most, cases its results for organic carbon may, with proper precautions, be made more valuable than the indications of the permanganate process, and its results for organic nitrogen in like manner more valuable than the indications of the albuminoid-ammonia process.

SPECIAL CONCLUSIONS AS TO THE ALBUMINOID-AMMONIA PROCESS.

These may be briefly summed up as follows:

1. In the determination of both "free" and "albuminoid" ammonia there is a loss, which may be quite considerable, resulting from imperfect condensation of the ammonia during distillation. This loss varies in amount with the precise conditions under which the distillation is conducted, especially with the efficiency of the cooling apparatus and the time occupied in the process.

2. In the case of waters containing urea, and also other amidated bodies, such as the leucine and tyrosine occurring among the pro-

ducts of putrefactive decay, some ammonia is so easily formed from these substances by boiling with sodium carbonate, or even without this addition, that it is impossible to distinguish sharply between pre-existing "free" ammonia (of ammoniacal salts), and that formed by the action of alkaline permanganate, the so-called "albuminoid" ammonia. This source of error as to the free ammonia reacts, as has been noticed above, upon the result for organic nitrogen by the combustion process.

3. There is no satisfactory evidence in favor of Wanklyn's view that in distilling with alkaline permanganate, definite and simple fractions of the nitrogen of organic matter are given off as "albuminoid" ammonia. Such results may be varied at pleasure, for most, if not for all substances, by slight modification of the conditions under which the distillation is conducted.

4. If the distillation with alkaline permanganate be carried out as usual, in accordance with Wanklyn's instructions, it frequently happens that the nitrogenous organic matter is so gradually acted upon as to make the ending of the process indefinite; ammonia is still coming off when the distillation has to be stopped in consequence of the contents of the retort being nearly reduced to dryness. In such cases an unknown fraction of the possible amount of albuminoid ammonia fails to be collected, and is but vaguely indicated by the sign + after the figures recorded.

5. There is evidence that in some cases nitrogenous organic matter is volatilized during the distillation for free ammonia, which, if it had been retained, would have yielded up its nitrogen as albuminoid ammonia; not affecting the Nessler reagent, such nitrogenous matter escapes detection under either head.

6. The albuminoid-ammonia process proper, *i. e.* the distillation with alkaline permanganate and determination of the ammonia evolved, is admittedly simple and easily carried out with very little preparatory training.

7. The value of the results by this process depends more upon watching the *progress* and *rate* of evolution of the ammonia than upon determining its total amount.

8. Taking the results by this process as recorded, we find a good deal of general similarity between the figures for albuminoid ammonia and those for organic nitrogen (by the combustion process), but with frequent discrepancies of varying extent, such as prevent the one being taken as the accurate measure of the other. See Tables XIX and XX, further on.

SPECIAL CONCLUSIONS AS TO THE PERMANGANATE PROCESS.

The chief points worthy of attention are the following:

1. The results obtained by the Tidy method (using the acidified permanganate at common temperature) and by that of Kubel (operating at the boiling point) differ irregularly from each other, the latter usually giving much higher figures, as was to be expected, but the ratio between the results by the two methods varies much in different cases.

2. On the whole, there seems usually to be a nearer approach to proportionality with the quantities of organic carbon[1] found by the combustion process on the part of the results afforded by the Kubel process than on that of the Tidy results, but to this there are some very notable exceptions. See, on this point, Tables XIX and XX, further on.

3. In a good many instances the results obtained by the Kubel method are, contrary to the general rule, lower than those afforded by the Tidy method. This seems to be due, in all probability, to loss of organic matter by volatilization with the escaping steam from the boiling liquid before time has been afforded for action on the permanganate.[2] An examination of all the results obtained for Nos. 131, 132 and 133, and several other cases, gives good ground for believing this to be the case. Of course, a similar loss may have occurred in other instances, but not to the extent of reversing the general rule as to the results by the Kubel process being larger than those by the method of Tidy; and this may in part explain the absence of any uniform ratio between the figures yielded by those two modifications of the permanganate process.

4. The results obtainable by the Tidy process are liable to variation with the atmospheric temperature prevailing at the time the process is applied.

[1] This appears to be the proper way of comparing the results of the permanganate with those of the combustion process. The former process is clearly concerned much more with carbon than nitrogen, if oxygen be usually at all consumed by nitrogen. It is not easy to admit the soundness of the logic with which Tidy (Jour. Chem. Soc. (Lond.), Jan. 1879, 94-97) points to the concordance of results, by the permanganate and combustion processes, and the disagreement with both these of the results by the albuminoid-ammonia process, and hence apparently infers that the two former are trustworthy, and the last not so. He uses the *sum of organic carbon and nitrogen* to represent the results by the combustion process, and as the carbon forms generally much the larger part of this, he naturally arrives at an agreement with the results of the process mainly depending on the oxidation of carbon, and disagreement with those of the process evolving nitrogen as ammonia.

[2] It is worthy of remark that the largest number of cases among natural waters of the Kubel process giving a lower result than that by the Tidy process occur among the waters believed to be *dangerous*, *i. e.* Class II.

5. The amount of oxygen consumed by a specimen of water is probably in all ordinary cases much below that required for complete oxidation of the organic matter present, and does not stand in any fixed ratio thereto; it cannot be taken as a measure either of the organic carbon or of the total organic matter. Nevertheless, a distinct general resemblance may be traced between strongly marked results, high or low, as the case may be, for the consumption of oxygen on the one hand, and organic carbon (by the combustion process) on the other; and closer agreement is observable in regard to waters of generally similar character.[1]

6. The permanganate process is capable of giving more valuable information in regard to a water by watching the *progress* and *rate* of the oxidation of organic matter present than by any single determination of the absolute amount of oxygen consumed in a given time.

7. For such observation of the progress of oxidation the two determinations prescribed by Tidy, viz. of oxygen consumed in one hour and in three hours, respectively, are not sufficient, nor is the latter period of three hours long enough to indicate the general behavior of the water with acid permanganate.

GENERAL REMARKS ON OTHER CHEMICAL DETERMINATIONS.

1. The determinations of total solids left on evaporation, of the loss on ignition of this solid residue, and even of chlorine, in the series of varied dilutions of identical or nearly identical liquids, show discrepancies which illustrate the comparative roughness of the methods by which these results were obtained when very small quantities have to be dealt with.[2] The evaporation of 100 cc. of water usually left a residue, the absolute weight of which was but a few milligrams, and a very little difference in the dryness attained, or in the atmospheric deposition on the surface of the platinum capsule, involved relatively large errors in the result. Even the volumetric processes for chlorine are far inferior in delicacy to those employed for the organic constituents.

2. As regards the results for nitrites and nitrates, the coincidence seems to be worth noting, which is often presented between alkaline

[1] In accordance with the remarks of Frankland: "Water Analysis," p. 55.

[2] It is true that Dr. Smart took no very special pains with these determinations, which were looked upon merely as incidental to the main object, checking to some extent the information as to the general character of each water. Still, this part of the work was done with fully average ordinary care.

reaction of a water and the occurrence of these salts in considerable or large quantity, suggesting as this does a recollection of the conditions under which nitrates are produced on the large scale in the decay of nitrogenous organic matter. The coincidence, however, is not always observable, nitrites and nitrates occurring pretty largely in some cases without alkaline reaction, while in other instances (as Nos. 89, 90 and 91, containing the washings from starch manufacture) there was alkaline reaction, and also much nitrogenous matter, but no nitrites or nitrates. Mr. Noyes has drawn my attention to the fact that in the waters containing large amounts of nitrates, ammonia appears in but small proportion; hence ammonium nitrate seems to be rare, the basic constituent being rather for the most part non-volatile—no doubt calcium, magnesium, or one of the alkaline metals; this is worth notice in relation to possible reduction to nitrite and consequent loss of nitrogen in the combustion process. The view of Frankland that nitrites are producible in water by the reducing action of organic matter upon nitrates[1] is clearly sustained by the results for Nos. 64 and 65, these representing a water originally containing nitrates to which different amounts of an infusion of hay had been added; it seems by no means established that nitrites are *always* developed by reduction, some of Dr. Tanner's experiments which have been reported indicating that on the contrary these salts may be produced by oxidation, which, if it go on, leads to the formation of nitrates. Frankland's view, also, that nitrates are not found in waters deficient in dissolved oxygen, is in general accordance with the results obtained in this investigation, though there are a few instances—Nos. 20, 27, 43, and notably 33—in which nitrates are present to a considerable extent in waters with less than a full proportion of free oxygen in solution.

3. The experiments with tannin simply serve to show how utterly worthless is this "group-reagent" of Kämmerer for the purpose for which he has advocated its use.

4. The general series of analyses of the dissolved gases confirms what has been said on previous pages of the general report as to the number of varying conditions which influence the results in this direction—oxidizability of organic matter present, temperature, extent of exposure to the atmosphere, and interchange with it in both directions of gaseous constituents. In a number of cases the

[1] "Water Analysis," pp. 28 and 42.

consumption of dissolved oxygen, and production in its place of carbon dioxide from the carbon of organic matter is very obvious, but the extent to which this is found going on varies greatly, and is masked by the escape to a greater or less extent of the latter gas and reabsorption from the air of the former. The conclusion of Weyl and Zeitler,[1] from a few experiments, that the quantity of free oxygen in solution does not bear any fixed ratio to the quantity of acidified permanganate decolorized by a water, is sustained by many of the specimens in the main series, as for instance, Nos. 60 to 80, inclusive. Nevertheless, it may be well to include an examination of the dissolved gases in the study of any water in regard to which the fullest chemical information is desired. In such a case the examination ought to be made with the least possible interval of time after collection of the sample, and preferably on the spot where the sample is taken, with observation of the temperature of water and air.

MICROSCOPICAL AND PATHOLOGICAL RESULTS.

Feeling my own incompetence properly to discuss these, I prefer to leave them to speak for themselves, except so far as Professor Martin has, as quoted in a previous part of the general report, given his views as to the methods employed and the general significance of the facts recorded—these views having been formed, however, while he still was ignorant of the history of the individual waters.

It may be said, I think, that the microscopic and culture observations indicate at the same time the real importance of connecting with a chemical examination of water a study in competent hands of its microscopic organisms both as to number and kind, and also the difficulty often presented, either by the sparseness or more frequently the abundance of these organisms, in fairly estimating their average relation to the mass of the water. This difficulty is superadded, of course, to the imperfection of our knowledge as to the effects upon human health of some closely allied—even hardly distinguishable—organisms, of dangerous and harmless associations, and of perhaps the same organism in different stages of its life history. The probable general significance of certain large classes of organized forms seems, however, well established, and well worthy of attention.

[1] Zeitschr. f. phys. Chem. 5, 10 (1880).

It may also be said of the pathological experiments with rabbits, that, opening up as they do a new and almost untried field of research, they show the great complexity of conditions to be encountered, the necessity of careful attention to details, and of multiplying and varying such experiments as far as possible, and the caution which must be exercised in drawing generalized conclusions from them; but on the other hand the results so far obtained, many of which individually are exceedingly suggestive, seem to indicate that real value attaches to this method of investigation, not in the direction proposed by Emmerich (as a part of the ordinary examination of a drinking-water, in order to determine directly its wholesomeness or the reverse), but as the means in part of arriving at trustworthy grounds for the interpretation of chemical and microscopical results.

(*To be continued.*)

Contributions from the Chemical Laboratory of Harvard College.

XXIV.—ON CERTAIN TETRASUBSTITUTED PROPIONIC ACIDS.

By Henry B. Hill and Charles F. Mabery.

In a previous communication[1] one of us has already mentioned the fact that the dibromacrylic from mucobromic acid, unlike the dichloracrylic acid of Wallach, takes up a molecule of bromine with readiness and forms a tetrabrompropionic acid. We were led to undertake a more complete study of the tetrasubstituted propionic acids, especially with the hope that the study of those containing two different halogens might throw some light upon the position of the halogen atoms in the disubstituted acrylic acids formed from mucobromic and mucochloric acids. After our investigations were concluded, Mauthner and Suida[2] published in the Proceedings of the Vienna Academy a paper entitled "Ueber gebromte Propionsäuren und Acrylsäuren," in which they antici-

[1] This Journal **3**, 116; and Proceedings American Academy, **16** (N. S. viii), 197.

[2] Sitzungsberichte der kk. Akademie Wien, **83**, 273.

pate us in the publication of a portion of our work. Since they were perfectly well aware that, in studying derivatives of a substituted acrylic acid which they asserted, although without adequate proof, was identical with that obtained from mucobromic acid, they were trespassing upon ground which one of us had already fully reserved, we think it advisable, although it involves a certain amount of repetition, to give our results in full, more especially since we are able to correct their work in several important particulars.

Tetrabrompropionic Acid.

Tetrabrompropionic acid can readily be made by the addition of bromine to dibromacrylic acid at ordinary temperatures.[1] We have prepared it by adding to a solution in chloroform the calculated amount of bromine. On standing, the addition product gradually separates, often in large, well-formed prisms. The amount of the product thus obtained was about 90 per cent. of the theoretical yield. After recrystallization from chloroform the substance was dried over sulphuric acid.

I. 0.5480 gram substance gave 0.1837 gram CO_2 and 0.0286 gram H_2O.

II. 0.1775 gram substance gave 0.3432 gram AgBr.

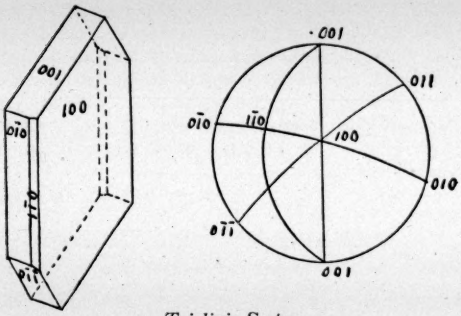
	Calculated for $C_3H_2Br_4O_2$.	Found.	
		I.	II.
C	9.23	9.14	...
H	0.51	0.58	...
Br	82.04	...	82.28

Tetrabrompropionic acid crystallizes in prisms of the triclinic system, which melt at 125–126°. It is very soluble in alcohol or ether, readily soluble in hot chloroform, carbonic disulphide or benzol, and separates in crystals as these solutions cool. In ligroin it is sparingly soluble. Under water it melts at a very low temperature to a colorless oil which dissolves freely on heating.

For a crystallographic study of the substance we are indebted to Dr. W. H. Melville.

[1] Mauthner and Suida assert that the dibromacrylic acid will take up no bromine in the cold. They prepared tetrabompropionic acid by heating to 100° with undiluted bromine. That the bromine is very readily taken up one of us first mentioned several years ago (Berichte der deutsch. chem. Gesellsch. **12**, 657).

CRYSTALLINE FORM OF TETRABROMPROPIONIC ACID.



Triclinic System.

Forms, [100] [010] [001] [011] [110].

Elements: Macrodiagonal $a = 1.507$
Brachydiagonal $b = 1$
Vertical axis $c = 0.934$
Angles of axes $XY = 94°59'$
$XZ = 104°28'$
$YZ = 74°20'$

Angles between Normals.

	Observed.	Calculated.
100 and 010	$= 88°\ 48'$	
010 " 011	$= 56°\ 3'$	
011 " 001	$= 48°\ 51\frac{1}{2}'$	Fundamental angles.
100 " 011	$= 77°\ 21\frac{1}{2}'$	
100 " 110	$= 57°\ 25'$	
100 " 001	$= 77°\ 1'$	$76°\ 21'$

Argentic Tetrabrompropionate, $AgC_3HBr_4O_2$. Argentic nitrate added to a solution of the acid in dilute alcohol precipitates the silver salt in clustered needles, which may further be increased in quantity by the cautious addition of ammonic hydrate. The salt is extremely unstable, forms argentic bromide on warming, and blackens rapidly in diffused light.

1.2182 gram of the salt dried over H_2SO_4 gave 0.4744 gram AgBr.

	Calculated for $AgC_3HBr_4O_2$.	Found.
Ag	21.78	22.38

Baric Tetrabrompropionate, $Ba(C_3HBr_4O_2)_2 . 2H_2O$. An aqueous solution of the acid dissolved baric carbonate rapidly in the cold, and if the solution was not warmed there was no noticeable decomposition. On spontaneous evaporation at ordinary temperatures the barium salt was left in clusters of flattened needles. When dried by exposure to the air they contained two molecules of water, which they lost over sulphuric acid.

I. 0.7239 gram of the air-dried salt lost over H_2SO_4 0.0272 gram H_2O.

II. 0.7087 gram of the air-dried salt lost over H_2SO_4 0.0259 gram H_2O.

	Calculated for $Ba(C_3HBr_4O_2)_2 . 2H_2O$.	Found. I.	II.
H_2O	3.79	3.76	3.66

0.6756 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.1742 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_4O_2)_2$.	Found.
Ba	14.97	15.16

Calcic Tetrabrompropionate, $Ca(C_3HBr_4O_2)_2$. The calcium salt, made by neutralizing an aqueous solution of the acid with calcic carbonate and allowing the solution to evaporate spontaneously, crystallized in needles which proved to be anhydrous. The salt freed from moisture by pressure did not materially lose in weight when exposed to the air, and when air-dried lost nothing over sulphuric acid.

I. 0.5065 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.0888 gram $CaSO_4$.

II. 1.0886 gram of the salt dried over H_2SO_4 gave 0.1850 gram $CaSO_4$.

	Calculated for $Ca(C_3H_2Br_4O_2)_2$.	Found. I.	II.
Ca	4.89	5.16	5.00

When a solution of baric tetrabrompropionate was heated baric bromide was formed, carbonate dioxide escaped, and at the same time the liquid became turbid through the separation of a colorless oil.[1] On distilling the liquid the oil passed readily over with steam, and since from the method of its formation there could be little doubt that it was tribromethylen, for identification it was

[1] Mauthner and Suida assert that this decomposition also takes place on long standing at ordinary temperatures. They were therefore able to isolate no salts. We have never observed any decomposition in the cold. *Loc. cit.* p. 284.

immediately converted into its dibromide by the addition of bromine. The crystalline addition product which was thus obtained when purified by recrystallization melted at 53° and gave on analysis a percentage of bromine which showed it to be pentabromethan.

0.1696 gram substance gave 0.3766 gram AgBr.

Calculated for C_2HBr_5.	Found.
94.12	94.48

This decomposition may therefore be expressed by the equation:

$$Ba(C_3HBr_4O_2)_2 = BaBr_2 + 2CO_2 + 2\,C_2HBr_3.$$

By the action of an alcoholic solution of potassic hydrate upon tetrabrompropionic acid a molecule of hydrobromic acid is removed, and there results the tribromacrylic acid melting at 118° which we have already described.[1] Dr. W. H. Melville kindly made a crystallographic study of the crystals which we obtained, and established their identity with those he had previously examined, which were prepared by the addition of bromine to brompropiolic acid. A description of the crystalline form of tribromacrylic acid Dr. Melville presents in a separate communication.

a Dichlorbrompropionic Acid.

In studying the dichloracrylic acid made from mucochloric acid W. Z. Bennett and one of us found that even at 100° it would not take up bromine when dissolved in chloroform.[2] Subsequently it appeared from the experiments of C. W. Andrews that the substituted propionic acid could readily be made by the action of undiluted bromine, although circumstances at the time prevented a detailed study on his part. As a precise characterization of this addition product seemed of interest we undertook its preparation and investigation.

Pure dichloracrylic acid melting at 85–86° was heated with a molecule of bromine for several hours at 100°. The almost colorless product of the reaction was pressed thoroughly with paper and

[1] This Journal **3**, 178; and Proceedings American Academy **16** (N. S. viii), 216. Mauthner and Suida assign to the barium and calcium salts of this acid, prepared by them from tetrabrompropionic acid, formulae differing greatly from those which we formerly established by our analyses. Since their determinations were made with small quantities of material, we have not thought it necessary to make further analyses in support of our formulae.

[2] This Journal **3**, 172; and Proceedings American Academy, **16** (N. S. viii), 211.

purified by crystallization, at first from carbonic disulphide, and finally from chloroform. When dried over sulphuric acid this substance gave on analysis percentages agreeing closely with those required by the formula $CH_2Cl_2Br_2O_2$. In the indirect determination of the halogens we used the extremely convenient and accurate method recently described by Mr. L. P. Kinnicutt.[1]

I.[2] 0.8124 gram substance gave 0.3550 gram CO_2 and 0.0665 gram H_2O.

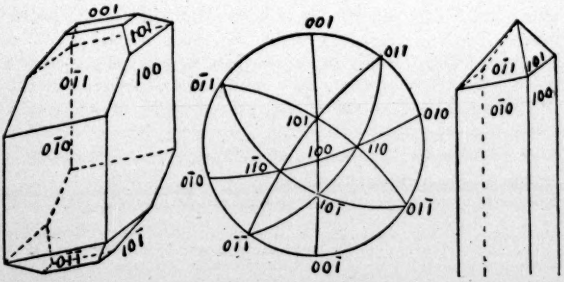
II. 0.1715 gram substance gave 0.3775 gram AgCl+AgBr.

III. 0.4790 gram substance gave 1.0559 gram AgCl+AgBr. From this by reduction was obtained 0.6887 gram Ag.

	Calculated for $C_3H_2Cl_2Br_2O_2$.		Found.		
			I.	II.	III.
C	11.96		11.91	...	...
H	0.67		0.90	...	...
Cl	23.59	76.74	...	76.93	23.77
Br	53.15				52.90

This *a* dichlordibrompropionic acid crystallizes in well-formed tricliuic prisms, which melt at 94–95°. It is readily soluble in water, alcohol, or ether; in carbonic disulphide, chloroform, or benzol it dissolves less freely. From a solution in carbonic disulphide it could be obtained by slow evaporation in well-formed crystals, whose study was kindly undertaken by Dr. W. H. Melville.

CRYSTALLINE FORM OF *a* DICHLORDIBROMPROPIONIC ACID.



[1] This Journal **4**, 22; and Proceedings American Academy, **17** (N. S. ix), 91.

[2] These analyses were made by Mr. Andrews.

Triclinic System.

Forms, [100] [010] [001] [101] [011] [10$\bar{1}$] [01$\bar{1}$]; [110] and [1$\bar{1}$0] often present.

[1] Elements: Macrodiagonal a = 1.023
Brachydiagonal b = 1
Vertical axis c = 1.052
Angles of axes XY = 91°
XZ = 76° 31½′
YZ = 108° 52′

Angles between Normals.

	Observed.	Calculated.
100 and 010	= 93° 37′	Fundamental angles.
100 " 101	= 52° 58′	
010 " 011	= 34° 57′	
010 " 101	= 77° 19′	
101 " 011	= 58° 46′	
100 " 10$\bar{1}$	= 38° 32′	38° 41′
011 " 001	= 35° 21′	35° 52′
001 " 01$\bar{1}$	= 55° 45′	55° 30′
100 " 011	= 101° 3′	100° 39′
100 " 0$\bar{1}$1	= 98° 49′	98° 38′
101 " 101	= 87° 34′	88° 20′
10$\bar{1}$ " 011	= 50° 32′	50° 30′

Argentic α Dichlordibrompropionate, $AgC_3HCl_2Br_2O_2$. The silver salt falls, on the addition of argentic nitrate to an aqueous solution of the acid, in flattened jagged needles which are readily decomposed by heat. They could, however, be dried over sulphuric acid without any essential decomposition, as is shown by the following analysis:

0.4885 gram of substance gave by precipitation with HBr 0.2231 gram AgBr.

	Calculated for $AgC_3HCl_2Br_2O_2$.	Found.
Ag	26.46	26.23

Baric α Dichlordibrompropionate, $Ba(C_3HCl_2Br_2O_2)_2$. The barium salt we made by neutralizing a cold aqueous solution of the

[1] Through an error the ratios of the fundamental parameters were originally given in the Berichte der deutsch. chem. Gesellsch. **14**, 1680: a : b : c = 1.034 : 1 : 1.062.

acid with baric carbonate. On evaporation at ordinary temperatures it crystallized in long branching needles, which when dried by exposure to the air did not lose materially in weight over sulphuric acid, and contained a percentage of barium corresponding to the anhydrous salt.

I. 0.5069 gram of the air-dried salt gave 0.1606 gram $BaSO_4$.

II. 0.5239 gram of the air-dried salt gave 0.1676 gram $BaSO_4$.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2$.	Found. I.	II.
Ba	18.59	18.58	18.81

The barium salt is decomposed by warming, its solution giving products similar to those obtained in the same way from tetrabrompropionic acid. This decomposition, however, we have not as yet studied further.

β Dichlordibrompropionic Acid.

Although dibromacrylic acid assumes a molecule of bromine so readily, we found at first great difficulty in preparing the corresponding addition-product with chlorine. If chlorine gas is passed into melted dibromacrylic acid it is gradually taken up and the melting-point of the acid is slowly changed. After long-continued action a considerable quantity of the dichlordibrompropionic acid is formed, but so contaminated with oily by-products that its purification is a matter of some difficulty. This addition of chlorine is, however, rapidly and neatly accomplished if the reaction is allowed to proceed in direct sunlight at 100°. When at this temperature the melted acid becomes nearly solid with separating crystals of the addition-product, the chlorination is interrupted. The product which we obtained in this way from pure dibromacrylic acid melting at 85–86° was purified by crystallization first from carbonic disulphide and finally from chloroform. On analysis it gave the following results:

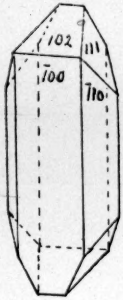
I. 0.5183 gram substance gave 0.2335 gram CO_2 and 0.0431 gram H_2O.

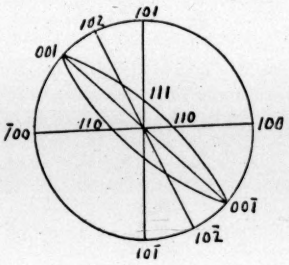
II. 0.1547 gram substance gave 0.3400 gram AgCl+AgBr. From this by reduction was obtained 0.2214 gram Ag.

	Calculated for $(C_3H_2Cl_2Br_2O_2)$.	Found. I.	II.
C	11.96	12.13	...
H	0.66	0.92	...
Cl	23.59	...	23.37
Br	53.15	...	53.21

This β dichlordibrompropionic acid crystallizes in oblique prisms which melt at 118–120°, and in its behavior with solvents closely resembles the α acid. In water, alcohol or ether it dissolves very easily, but with somewhat more difficulty in carbonic disulphide, chloroform, or benzol. The solution in carbonic disulphide gave by slow evaporation well-developed crystals whose elements Dr. W. H. Melville kindly determined.

CRYSTALLINE FORM OF β DICHLORDIBROMPROPIONIC ACID.





Monoclinic System.

Forms, [100] [110] [111] [102].

Elements: Clinodiagonal $a = 2.393$
Orthodiagonal $b = 1$
Vertical axis $c = 1.731$
Angle of axes $XZ = 46° 9'$

Angles between Normals.

	Observed.	Calculated.
110 and $\bar{1}10$ =	60° 11′	Fundamental angles.
111 " $\bar{1}10$ =	42° 24½′	
111 " 110 =	40° 33½′	
$\bar{1}00$ " $\bar{1}10$ =	59° 53′	59° 54½′
111 " $1\bar{1}1$ =	120° ½′	119° 56′
100 " $11\bar{1}$ =	88° 57′	88° 47′
102 " $\bar{1}10$ =	102° 21′	102° 23′
102 " 110 =	78° 5′	77° 37′
102 " 111 =	63° 44′	63° 42½′

The difference between the α and β acids was further confirmed by a study of the silver and barium salts.

Argentic β Dichlordibrompropionate, $AgC_3HCl_2Br_2O_2$. The silver salt is precipitated in the form of short, thick, pointed prisms when argentic nitrate is added to an aqueous solution of the acid. It is readily decomposed by heat, but may be dried for analysis over sulphuric acid.

0.4950 gram of the salt gave on precipitation with HCl 0.1731 gram AgCl.

	Calculated for $AgC_3HCl_2Br_2O_2$.	Found.
Ag	26.46	26.31

Baric β Dichlordibrompropionate, $Ba(C_3HCl_2Br_2O_2)_2 . 2H_2O$. The barium salt which we made by neutralizing an aqueous solution of the acid with baric hydrate, crystallized on spontaneous evaporation of its solution in long radiating needles which were very soluble in cold water. When dried by exposure to the air the salt proved to contain two molecules of water which it lost over sulphuric acid.

I. 1.6201 gram of the air-dried salt lost over H_2SO_4 0.0705 gram H_2O.

II. 1.5443 gram of the air-dried salt lost over H_2SO_4 0.0731 gram H_2O.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2 . 2H_2O$.	Found.	
		I.	II.
H_2O	4.66	4.35	4.74

0.8236 gram of the salt dried over H_2SO_4 gave 0.2616 gram $BaSO_4$.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2$.	Found.
Ba	18.59	18.69

These results prove that the α and β dichlordibrompropionic acids described are essentially different.

	Dichlordibrompropionic Acid.	
	α	β
System of Crystallization	Triclinic.	Monoclinic.
Melting-point	94–95°	118–120°
Barium salt	$Ba(C_3HBr_2Cl_2O_2)_2$	$Ba(C_3HBr_2Cl_2O_2)_2 . 2H_2O$.

The barium salt was readily decomposed by warming its aqueous solution. Baric chloride and carbonic dioxide were formed together with a colorless oil which undoubtedly was a dibromchlorethylen. With bromine this oil gave a solid addition product, which, however, we have not as yet prepared in quantity sufficient for complete purification and identification.

XXV.—ON THE CONSTITUTION OF THE SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

By Henry B. Hill.

Within a few years the number of substituted acrylic and propionic acids known has been largely increased, and yet the constitution of but few of these can be said to be satisfactorily established. In a previous communication I was led to adopt provisionally for mucobromic acid the formula—

$$\begin{array}{l} CBr_2 - CHO \\ | \\ = C - COOH \end{array}$$

which explained its connection with maleic acid, in whose molecule the researches of Fittig had shown the probable existence of a dyad carbon atom. The structure of the related dibromacrylic acid was then naturally expressed by the formula—

$$\begin{array}{l} CBr_2H \\ | \\ C = \\ | \\ COOH \end{array}$$

against which at the time nothing more convincing than a belief in its improbability could be urged. The relations which Andrews and I have shown to exist between this same acid and two different tribrompropionic acids prove, however, that this formula is incorrect. An acid with this structure could be formed from but a single tribrompropionic acid, and must of necessity give this same tribrompropionic acid by the addition of hydrobromic acid. The same objection also applies with equal force to the other two conceivable formulae for dibromacrylic acid which contain dyad carbon—

$$\begin{array}{l} = CH \\ | \\ CBr_2 \\ | \\ COOH \end{array} \qquad \text{and} \qquad \begin{array}{l} = CBr \\ | \\ CHBr \\ | \\ COOH \end{array}$$

and these must consequently be rejected. There remain therefore for the acid in question but two possible formulae—

$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array} \qquad \text{and} \qquad \begin{array}{l} CHBr \\ \| \\ CBr \\ | \\ COOH \end{array}$$

The formation of two isomeric dichlordibrompropionic acids by the addition of chlorine to the dibromacrylic acid and of bromine to the analogous dichloracrylic acid, as Mabery and I have shown, would seem again to be decisive in favor of the first of these formulae, since its adoption would give—

$$\begin{array}{l} CBr_2Cl \\ | \\ CHCl \\ | \\ COOH \end{array} \qquad \text{and} \qquad \begin{array}{l} CCl_2Br \\ | \\ CHBr \\ | \\ COOH \end{array}$$

as the structure of the two isomeric dichlordibrompropionic acids, while the second formula would give in either case the same compound—

$$\begin{array}{l} CHBrCl \\ | \\ CBrCl \\ | \\ COOH \end{array}$$

Although it was by no means impossible that a molecular rearrangement had taken place in one of these two reactions, still it seemed improbable, since the reactions were apparently neat, and in the treatment with chlorine, where such a change would be more naturally expected, no bromine could be detected in the escaping chlorine. On the other hand the adoption of the formulae—

$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array} \qquad \text{and} \qquad \begin{array}{l} CCl_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

for the derivatives of mucobromic and mucochloric acids presented difficulties quite as serious. In the first place the dichloracrylic acid of Wallach had been proved beyond all doubt to be different from that which Bennett and I had described by a comparison of the crystalline form of the two acids, and it would follow then that Wallach's acid could not have the formula he assigned to it. The formation of an acid with different structure from chloralid could, however, be explained upon the assumption that the chlorpropiolic acid was the first product of the reduction, and that this passed, on the one hand by the addition of hydrogen, into the β chloracrylic acid, and on the other hand formed dichloracrylic acid by addition in the subsequent treatment with strong hydrochloric acid which

Wallach prescribes.[1] Although this hypothesis was far from satisfactory, it seemed to me hardly more improbable than that a similar molecular rearrangement had taken place in the reaction which had come under my own observation.

Still another difficulty was to be found in the formation of the dibromacrylic acid in question from the tribrompropionic acid melting at 92°, which, if the ordinarily accepted formula for the latter—

$$\begin{array}{l} CH_2Br \\ | \\ CBr_2 \\ | \\ COOH \end{array}$$

were correct, would prove the incorrectness of the formula assumed. I was at first unable to attach any great importance to this argument, inasmuch as the constitution of the monobromacrylic acids was extremely uncertain. For although the discovery by Wallach of the β monobromacrylic acid melting at 115° had rendered the constitution of the α and β monobromacrylic acids of Tolens extremely doubtful, it by no means proved their identity.

Erlenmeyer has, however, recently shown[2] that the α and β acids of Tollens, as well as their potassium salts, crystallize in identical forms, and the structure of the tribrompropionic acid melting at 92° is therefore put upon quite another footing. Since the same (α) monobromacrylic acids can be made from α dibrompropionic and also from its isomer, the α β dibrompropionic, it follows that this acid must have the structure—

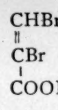
$$\begin{array}{l} CH \\ \| \\ CBr \\ | \\ COOH \end{array}$$

and the tribrompropionic acid made from it by the addition of bromine must of course have the corresponding form—

$$\begin{array}{l} CH_2Br \\ | \\ CBr_2 \\ | \\ COOH \end{array}$$

[1] Annalen der Chemie, **193**, 7.
[2] Berichte der deutschen chemischen Gesellschaft, **14**, 1867.

Since the formulae with dyad carbon are in this case excluded, there remains for the dibromacrylic acid in question only the structure—



Although this conclusion is directly at variance with the results which Mabery and I obtained in the study of the dichlordibrompropionic acids, it must be confessed, I think, that it is probably correct. Still, since its adoption presents undoubted difficulties, I shall endeavor to bring more direct experimental evidence as to its correctness.

The dibromacrylic acid of Fittig and Petri, which, as Mabery and I have shown, can be made from brompropiolic acid, would naturally have the form—

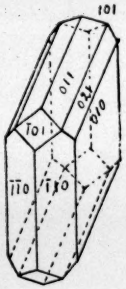
and the acids made in the same way containing two halogens the corresponding—

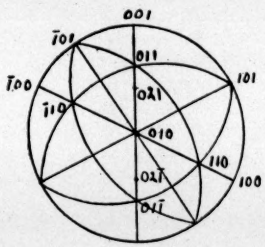
The tribrompropionic acid melting at 118° would be written—

and the tetrabrompropionic acid would have the form—

XXVI.—CRYSTALLINE FORM OF TRIBROMACRYLIC ACID.

By W. H. Melville.





Monoclinic System.

Forms, [010] [110] [011] [101] [$\bar{1}$01] [021]; the last three forms being rarely observed.

Elements: Clinodiagonal $a = 0.502$
Orthodiagonal $b = 1$
Vertical axis $c = 0.559$
Angle of axes $XZ = 64° 29\frac{1}{2}'$

Angles between Normals.

	Observed.	Calculated.
010 and $\bar{1}10$	$65° 38'$	Fundamental angles.
010 " 011	$63° 14'$	
011 " 110	$57° 35'$	
$\bar{1}10$ " $\bar{1}\bar{1}0$	$48° 42'$	$48° 44'$
010 " 021	$44° 41'$	$44° 45'$
021 " 011	$18° 33'$	$18° 29'$
011 " $0\bar{1}1$	$53° 33'$	$53° 32'$
011 " $\bar{1}01$	$42° 25'$	$42° 23\frac{1}{2}'$

Since[1] Dr. F. Becke's results of the determination of the same crystals do not appear to be reconcilable with the above, a com-

[1] Sitzungsberichte der kaiser. Akad. der Wissensch. **83**, 286, 287, Wien, 1881.

parison is important. The forms r (110) l ($1\bar{1}0$) when referred to the crystals which I have examined, correspond to [021], and o ($\bar{1}11$), u ($\bar{1}\bar{1}1$) would, if present, occur as the prism [120]. Among the many sets of crystals submitted to me I have never observed the prism [120]. The following table shows a few of the angles both actual and hypothetical, assuming that the crystals are monoclinic in form, when compared with Becke's corresponding measurements.

Monoclinic.	Becke.
$(010) \wedge (021) = 44° 41'$	$44° 42' = br$
$(021) \wedge (0\bar{2}1) = 90° 38'$	$91° 11' = rl$
$(0\bar{2}1) \wedge (0\bar{1}0) = 44° 41'$	$44° 13' = bl$
$(010) \wedge (\bar{1}20) = 47° 45\frac{2}{3}'$	$47° 19' = bu$
$(\bar{1}20) \wedge (\bar{1}\bar{2}0) = 84° 28\frac{2}{3}'$	$84° 55' = ou$
$(\bar{1}\bar{2}0) \wedge (0\bar{1}0) = 47° 45\frac{2}{3}'$	$48° 10' = bo$
$(010) \wedge (020) = 44° 41'$	$44° 27\frac{1}{2}' =$ mean of br and bl
$(010) \wedge (120) = 47° 45\frac{2}{3}'$	$47° 44\frac{1}{2}' =$ " " bu " bo

The following measurements, which were obtained from a single crystal, appear to establish conclusively the system of crystallization as monoclinic.

Zone [010, 110]

$(110) \wedge (010) = 65° 33'$
$(010) \wedge (\bar{1}10) = 65° 44'$
$(\bar{1}10) \wedge (\bar{1}\bar{1}0) = 48° 28'$
$(\bar{1}\bar{1}0) \wedge (0\bar{1}0) = 65° 52\frac{1}{2}'$
$(0\bar{1}0) \wedge (1\bar{1}0) = 65° 35'$
$(1\bar{1}0) \wedge (110) = 48° 44'$

$359° 56\frac{1}{2}'$

Zone [010, 011]

$(010) \wedge (021) = 44° 41'$
$(021) \wedge (011) = 18° 30'$ } $63° 11'$
$(011) \wedge (0\bar{1}1) = 54° 5'$
$(0\bar{1}1) \wedge (0\bar{1}0) = 62° 56'$

$180° 12'$

$(1\bar{1}1) \wedge (011) = 122° 32\frac{1}{2}'$
$(011) \wedge (\bar{1}10) = 57° 18\frac{1}{2}'$

$179° 51'$

$(0\bar{1}1) \wedge (\bar{1}\bar{1}0) = 57° 2\frac{1}{2}'$

The crystal face (011) was somewhat imperfect, so that the reflected image was extended in width. Hence, the angles between (011) and adjacent planes are rendered uncertain, but only by the small value of 7′ or 8′. All the other faces gave exceedingly sharp reflections.

From these considerations upon the system in which tribromacrylic acid crystallizes, it will appear that we have to deal with a question of small differences, and that in consequence of the very prominent monoclinic habit, we are justified in making these crystals monoclinic, and not triclinic, as Becke has determined them.

DETERMINATION OF BORACIC ACID.

By Edgar F. Smith.

When a solution of manganese sulphate is added to one of borax, and to this mixture an equal volume of alcohol, there separates rapidly a white flocculent precipitate of manganese borate, MnB_4O_7, insoluble in the alcoholic liquid. The excess of manganese sulphate remains in solution, and can readily be determined in the filtrate from the borate after the expulsion of the alcohol. To ascertain whether the above might be available quantitatively, the following solutions of definite strength were prepared and the experiments recorded.

1. A solution of manganese sulphate, made by dissolving 3 grams of anhydrous $MnSO_4$ in 250 cc. H_2O. 10 cc. of this solution would then correspond to .0600 gram $MnSO_4$.

2. Potassium permanganate solution of such strength that 18.5 cc. were equivalent to 10 cc. of I or 1 cc. $KMnO_4 = .00324$ gram $MnSO_4$.

3. Borax solution: 10 grams well crystallized borax dissolved in 1 litre of H_2O.

The manner of conducting each experiment was as follows: To 10 cc. of the borax solution were added 10 cc. $MnSO_4$ solution and an equal volume of strong alcohol. The whole was well mixed, allowed to stand, carefully covered, for one half-hour, when the manganese borate was filtered rapidly (best with a suction

pump), and washed well with alcohol. The filtrate and washings were placed in a platinum or porcelain dish and evaporated to dryness on a water-bath. The residual manganese was then determined according to Volhard's method[1] by dissolving it in water, adding zinc sulphate, then heating to almost boiling, and carefully running in potassium permanganate until the liquid assumed a pink color. The quantity of manganese sulphate thus found and deducted from the whole amount of the salt added, gave a difference representing the manganese sulphate which had combined with the borax. After calculating the amount of manganous oxide to which the sulphate, found by difference, is equivalent, the following equations were employed:

$MnO : 2B_2O_3 :: $ am't MnO : corresponding am't B_2O_3 (x);

and

Orig. sub. 10 cc. borax solution : x :: 100 : y (per cent. B_2O_3 in 10 cc. of the borax solution).

Experiments.

Number of Anal.	Borax solution used.	$MnSO_4$ solution added.	No. cc. $KMnO_4$ requ'd for excess of $MnSO_4$	$MnSO_4$ in excess.	$MnSO_4$ in combination with B_2O_3.	Per cent. found of B_2O_3.
1	10 cc.	10 cc.	6.4 cc.	.0207 gram	.0393 gram	36.44
2	"	"	6.1	.0198	.0402	37.27
3	"	"	6.3	.0204	.0396	36.71
4	"	"	6.3	.0204	.0396	36.71
5	"	"	6.5	.0210	.0390	36.16
6	"	"	6.4	.0207	.0393	36.44
7	"	"	6.5	.0210	.0390	36.16
8	"	"	6.4	.0207	.0393	36.44
9	"	"	6.2	.0201	.0399	36.99
10	"	"	6.3	.0204	.0396	36.71
11	"	"	6.3	.0204	.0396	36.71
12	"	"	6.4	.0207	.0393	36.44
13	"	"	6.5	.0210	.0390	36.16
14	"	"	6.3	.0204	.0396	36.71
15	"	"	6.4	.0207	.0393	36.44
16	"	"	6.3	.0204	.0396	36.71
17	"	"	6.5	.0210	.0390	36.16
18	"	"	6.4	.0207	.0393	36.44

The calculated percentage of B_2O_3 in borax is 36.60, and from the experimental results it will be observed that the method can be successfully applied in the analysis of soluble borates.

[1] Annalen der Chemie, **198**, 318.

In estimating the boracic acid in insoluble borates, as tourmaline, the following course was pursued. The finely pulverized substance was fused with a weighed quantity of pure sodium carbonate, the fused mass exhausted with water, and to the filtrate containing all the sodium borate, together with some sodium silicate and aluminate, was added an amount of pure ammonium sulphate molecularly equivalent to the sodium carbonate. The solution was then digested until all the ammonia was expelled and the volume of the liquid largely reduced. Any silicic acid or aluminum hydrate which had separated was now filtered off, and the precipitate thoroughly washed with hot water. The solution, again reduced in volume and containing only the borate and sulphate of sodium and excess of ammonium sulphate, was mixed with a definite amount of a manganese sulphate solution (strength previously determined), alcohol added, and after standing one half-hour the borate was removed by filtration, the filtrate evaporated to dryness and the residue carefully ignited to expel the ammonium salt. The manganese sulphate left was dissolved in water, and the same procedure as indicated in the preceding experiments was carried out.

In a specimen of tourmaline from New York the boracic acid found by this method was 9.70 per cent. Another portion of the same material with Marignac's method[1] yielded 10 per cent. B_2O_3. In another tourmaline (locality unknown) two determinations by this method gave 6.55 per cent. B_2O_3 and 6.32 per cent. B_2O_3, while with Marignac's method the amount obtained was 6.80 per cent. B_2O_3.

In some instances upon evaporating the alcoholic solution preparatory to determining the excess of manganese sulphate, brownish flocks separated. These were always dissolved in a little sulphuric acid and then evaporated to dryness.

The writer is under many obligations to Messrs. N. Wiley Thomas, S. B., and W. H. Jarden, S. B., for their assistance in the execution of the details of the above method.

MUHLENBERG COLLEGE, ALLENTOWN, PA., *June* 26, 1882.

[1] Zeitschrift für analyt. Chemie, **1**, 405.

Contributions from the Chemical Laboratory of Rutgers College.

VII.—ON THE REDUCTION OF FERRIC SOLUTIONS.

By Peter T. Austen and Geo. B. Hurff.

Although numerous volumetric methods have been proposed and used for determining iron, there seems to be none that possesses the simplicity, accuracy and elegance of the titration with potassium permanganate. In the analysis of iron ores by the use of this method, however, there are a few steps which are still open to improvement.

The remarkable discovery of Zimmermann,[1] that the addition of manganese sulphate to solutions of ferrous chloride entirely prevents the liberation of chlorine on the addition of potassium permanganate, thus making it possible to titer directly in a chlorhydric acid solution, has relieved the analysis of iron ores of one of its most irksome steps, the conversion of the chlorhydric acid solution into the sulphuric acid solution preparatory to reduction and titration with potassium permanganate.

The only remaining objection has been that the reduction of the ferrous solutions is liable to be unsatisfactory, either from incompleteness, danger of loss, or the length of time demanded. The reduction by zinc is objectionable because the zinc is liable to be impure, containing carbon or iron. A control determination of the iron can of course be made, and the amount introduced into the analysis deducted, but this is a method never advisable in analysis if it can be avoided, and in this case also increases the amount of work. If the solution is heated, oxidation easily takes place at the end of the reduction when all the zinc has been dissolved, while if an excess of zinc is used it takes time to dissolve the excess. If the excess is not dissolved, metallic iron may be precipitated.[2] Rose-Finkener[3] suggest having the solution dilute and hanging a little stick of zinc in it by means of platinum wire, but it is doubtful if this method is very practical. The use of zinc dust as recommended by R. Drown[4] appears to us to be open to the objection just stated in regard to ordinary zinc, viz. that it often contains iron, thus rendering control determinations, deductions

[1] Ber. d. d. chem. Ges. **14**, 779.
[2] Mitscherlich, Zeit. anal. Chem. **2**, 72.
[3] Rose, Quant. Anal. 1871, 100.
[4] Zeit. anal. Chem. **18**, 98.

and extra labor necessary. It is claimed for amalgamated zinc and platinum as an advantage that only pure zinc is dissolved, the impurities not passing into solution. A weighty objection to this method is, however, that so much time is lost by it. The reduction in this way always takes several hours; in fact, one recent text-book[1] directs twenty-four hours. Magnesium reduces well, but has the disagreeable property of floating on the surface. The reduction with hydrogen sulphide[2] requires a tedious evaporation.

It was our endeavor, therefore, to find some method by which ferric solutions could be quickly reduced and which would require no corrections. The following procedure was found to answer admirably.

The ferric chloride solution, which should contain about 5–10 cc. of free chlorhydric acid and about 0.1 gram of metallic iron in 100 cc., is placed in a 300 cc. flask with a long neck, diluted to 200 cc. and heated nearly to boiling. The heat is then removed, and a saturated solution of sodium sulphite is added in small amounts (about one cc. at a time) till 15–20 cc. in all have been used. While adding the sulphite, it is well to give the ferric solution a revolving motion by gently twirling the flask. The solution becomes colorless, showing that all the ferric chloride is reduced to ferrous chloride. The sodium sulphite which we use is obtained by recrystallizing the pharmaceutical article, and forms beautiful crystals which are perfectly free from iron. As soon as the solution of the sulphite has all been added, a rubber stopper and tube[3] are inserted, the pinch-cock *b* opened, and the liquid heated to boiling and kept at a brisk boil.

It is of course necessary that the last traces of sulphurous acid should be entirely expelled before titration, since any of it remaining would be oxidized by the permanganate and counted as iron. To ascertain if the steam is entirely free from sulphurous acid it is allowed to pass into a test-tube containing about 50 cc. of water to which a little sulphuric acid and a drop of potassium permanganate solution have been added. If there is the slightest trace of sulphurous acid in the steam the liquid will at once be decolorized. If the steam is allowed to pass for some time through this solution of permanganate, it will decompose it, but this does not interfere in any way with the sharpness of the test. As soon as the test

[1] Cairns' Manual of Quant. Anal., p. 45. [2] Fresenius, Quant. Anal., last Am. ed., p. 279.

[3] Fresenius, Quant. Anal., last Am. ed., p. 268, Fig. 51. In our apparatus, the right-hand tube is bent at about an inch from its junction with the rubber connection.

shows that the sulphurous acid has all been driven off, the end of the tube is washed off with a little hot water, the heat removed and the pinch-cock *b* closed. The end of the tube is allowed to dip into a beaker of cold distilled water. As soon as the flask has cooled enough to have a vacuum within it, which generally occurs in a few minutes, the clip is opened and the cold water allowed to run in in portions so as to thoroughly wash out the tube. The flask is allowed to fill till the liquid stands at about the beginning of the neck. The clip is then closed, the right-hand tube removed and the contents of the flask cooled[1] under the tap. The manganese sulphate is next added and the titration proceeded with.

The above method of procedure works as well with sulphuric acid solutions as with chlorhydric acid solutions. The reduction and titration together take from fifteen to twenty minutes. A number can of course be run at the same time. The following experiments show the accuracy of the method:

Subs. taken.	Weight taken.	Per ct. of Fe. found.	Per ct. of Fe. calc.	Difference.
Ammonium-Iron Alum,	1	11.529	11.618	—0.089 per ct.
Do.	1	11.649	"	+0.031 "
Ammonium-Ferrous Sulphate,	1	14.291	14.285	+0.006 "
Do.	1	14.291	"	+0.006 "

In another series of experiments 0.2 gram of pianoforte wire was dissolved in dilute chlorhydric acid, diluted to about 150 cc., oxidized with permanganate, the chlorine boiled off and then reduced in the manner described above. The titrations required the same number of cc. of permanganate as the same amount of the same iron used in setting the standard of the permanganate, viz. 16.5–16.6.

If iron alone is to be determined in an iron ore, it is not necessary to separate the silica when the ore is decomposed by chlorhydric acid. The very finely pulverized ore is simply boiled with concentrated chlorhydric acid till decomposed, the resulting liquid and silica washed into a flask and the solution reduced and titered as described. When it is necessary to use a flux it is advisable to separate the silica.

[1] To obtain sharp results by Zimmermann's method it is necessary that the solution should not be warm.

VIII.—NOTE ON THE PRECIPITATION OF STANNIC OXIDE FROM SODIUM STANNATE.

By Peter T. Austen.

When a solution of sodium stannate is acidified, stannic hydrate is precipitated according to the formula,

$$SnO(ONa)_2 + H_2SO_4 = SnO(OH)_2 + Na_2SO_4.$$

The precipitate dissolves on addition of an excess of the precipitant. The precipitated stannic hydrate is voluminous, flocculent and gelatinous, resembling aluminic hydrate. So far as I have been able to ascertain, no other decomposition of the stannate, than in the manner indicated, has been effected.

I was surprised to find that, on passing a stream of carbonic acid through a strong solution of sodium stannate containing an excess of sodium hydroxide, a dense, heavy, and rapidly subsiding precipitate of stannic oxide was formed, the reaction being

$$SnO(ONa)_2 + CO_2 = SnO_2 + Na_2CO_3.$$

The same precipitation occurs when, instead of carbonic acid, the solution of sodium stannate is boiled with pulverized sodium hydrogen carbonate. In this case the reaction is

$$SnO(ONa)_2 + 2NaHCO_3 = SnO_2 + H_2O + 2Na_2CO_3.$$

When dry, the precipitated SnO_2 forms a heavy white extremely fine powder. The reaction affords an excellent method of producing stannic oxide in quantity.

New Brunswick, N. J.

ON THE DETERMINATION OF THE FLASHING POINT OF PETROLEUM.

By John T. Stoddard.

If the best method known for determining boiling points gave trustworthy results only when size and shape of the retort, quantity of liquid and distance from surface of liquid to the vapor delivery tube conformed to certain rigid specifications—the results varying many degrees with a change in any one of these conditions—we

should feel not only that a method demanding such precision in apparatus and manipulation left much to be desired in these particulars, but also that the determinations obtained under such arbitrary conditions could be themselves but arbitrary and undeserving the name of true boiling points.

And yet until quite recently the best apparatus devised for finding the flashing point of petroleum presented similar and even more numerous disadvantages.[1] The flashing point as given by these instruments depends upon the size and shape of the oil holder, the quantity of oil, the means of ignition, and distance of the flame or spark from the surface of the oil, as well as upon a number of minor conditions. Agreement in the determinations of a given oil by means of a given tester demands skillful and painstaking manipulation; and agreement of different testers can apparently be secured only by selecting one as arbitrary standard and adopting conditions in the others which shall give corresponding results.

The attempt has evidently been made to simulate in these testers the conditions presented in the oil reservoir of a quietly burning lamp. But these conditions vary in every lamp, and in the same lamp at different times; moreover, it is not only in lamps as properly used and the cans and storage tanks of kerosene that explosions occur. Safety is insured only when we know that under no *possible* conditions, at the temperature to which it is liable to be exposed, can the oil evolve inflammable vapors. We should be able to determine the *minimum* flashing point, and the method should be as independent of external conditions as that employed for finding the boiling point.

The first suggestion of a principle by which this could be accomplished is due to V. Meyer.[2] It is saturation of air with vapor of the oil. Recognizing the promise of this principle, I have studied the methods proposed for its application, paying particular attention to that recently devised by Liebermann.[3]

In the method proposed by Meyer, as well as in the elaborate and clever apparatus of Haass,[4] the saturation of air with vapor is effected by shaking the oil in a closed vessel. Both are dependent for reliable results upon the interval of time allowed between the shaking and the testing. The shaking repeated from degree to

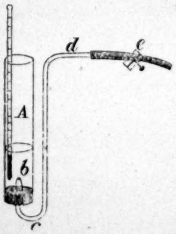
[1] Cf. Engler and Haass, Z. an. Chem. **20**, 1.
[2] Wagner's Jahresb. 1879, 1175, and Z. an. Chem. **20**, 28.
[3] Z. an. Chem. **21**, 321.
[4] Z. an. Chem. **20**, 29.

degree is an unpleasant feature of these methods. The apparatus of Haass can not be made in the laboratory and is expensive, costing, complete, 60 marks.

Liebermann's apparatus and method present none of these disadvantages. The air is saturated with vapor by being forced through the oil by pressure of a rubber bulb from degree to degree, while at the same instant a small flame is brought to the mouth of the oil holder. The apparatus has the recommendation of simplicity of construction and manipulation, and gives, as I have found, concordant results. Considerable care is, however, necessary to prevent spurting and regurgitation of the oil as the air current is suddenly started and interrupted. A continuous air current, Liebermann says, although simplifying the manipulation, raises the flashing point by preventing the accumulation of vapor enough for an explosion.

This statement I am unable to confirm, finding on the contrary that a continuous current of air, *if only rapid enough*, gives results identical with those of the intermittent method.

As result of my experiments I have adopted a modification of Liebermann's apparatus and method. The apparatus is shown in the cut. The cylinder is 2–3 cm. in diameter and 10–12 cm. long. Just within the wooden cork the small tube contracts to a fine orifice; at *d* it is connected by rubber tubing with a source of compressed air—small water blast, hand bellows or gasholder—the flow of which can be controlled by the pinch-cock *e*. Its use is as simple as its construction; *A* is about ⅓ filled with oil, and secured in a clamp at *d* so that it plunges in a water-bath to the level of the oil.[1] Air is now allowed to flow through *dcb*, and *e* adjusted so that about 0.5 cm. foam is maintained on the surface of the oil. From degree to degree the test is made by bringing a small blowpipe flame or a match for an instant to the mouth of *A*. At the flashing point the vapors ignite and the bluish flame runs down to the surface of the oil.



It is noteworthy that a *slow* continuous current of air gives a considerably higher flashing point. The rapid current is effective

[1] If plunged deeper than this, the sides of *A* above the level of the oil may become overheated, and, as they are constantly moistened by the foam, the flashing point is, in consequence, lowered. On this account I prefer a water to an air bath.

by bringing the vapor to the mouth of the tube and diluting it sufficiently to form an explosive mixture.

The results are very satisfactory, and the apparatus so simple that it can be made in ten minutes in any laboratory. Further important advantages are the ease of manipulation and readiness with which it can be thoroughly cleaned.

In all the apparatus suggested by Meyer's principle the determinations are largely independent of size or shape of oil holder, quantity of oil, means of ignition, distance of spark or flame from surface of oil and rapidity of heating, and in the form above described the determination of the flashing point becomes as easy and trustworthy an operation as that of determining the boiling point, while the results have a significance wholly wanting to those obtained by the older methods.

Determinations of Flashing-points.

1. Comparison of Liebermann's method with the above described modification:

	By L.'s method.			By the modification.		
Petroleum *A*	41	40.1	40.1	40	40	39.9
	40.5	40.5	40	40	40.1	40
Petroleum *B*		29			29	29

2. Influence of varying velocity of air-current:

Petroleum *A*.	Very slow,	43
	Slow,	41
	Fast enough to form 0.5 cm. foam	40
	Very much faster,	39.8 39.5 39.5

3. Influence of height of oil in holder:

Petroleum *C*.	Holder $\frac{1}{4}$ full	38.5
	" $\frac{1}{2}$ "	38.3
	" $\frac{3}{4}$ "	37.8

All determinations are in centigrade degrees.

SMITH COLLEGE LABORATORY, *Sept.* 4 1882.

FRIEDRICH WÖHLER.

No one but a chemist can appreciate the full significance of the brief message which came to us a month ago without warning—"Wöhler is dead!" What need be added to it? No chemist was better known or more honored than Wöhler, and none ever deserved distinction and honor more than he. His life was made up of a series of brilliant successes, which not only compelled the admiration of the world at large, but directed the thoughts of his fellow workers and led to results of the highest importance to science.

It is impossible in a few words to give a correct account of the work of Wöhler, and to show in what way his life and work have been of such great value to chemistry. Could he himself direct the preparation of this notice, the writer knows that his advice would be, "Keep to the facts." So far as any one phrase can characterize the teachings of Wöhler, that one does it; and though enthusiasm prompts to eulogy, let us rather recall the plain facts of his life, and let them, in the main, speak for themselves.[1]

He was born in the year 1800 at Eschersheim, a village near Frankfort-on-the-Main. From his earliest years the study of Nature appears to have been attractive to him. He took great delight in collecting minerals and in performing chemical and physical experiments. While still a boy he associated with a Dr. Buch of Frankfort, and was aided by this gentleman, who did what he could to encourage in the young student his inclination towards the natural sciences. The first paper which bears the name of Wöhler dates from this period, and is upon the presence of selenium in the iron pyrites from Kraslitz. In 1820 he went to the University of Marburg to study medicine. While there he did not, however, neglect the study of chemistry. He was at that time particularly interested in an investigation on certain cyanogen compounds. In 1821 he went to Heidelberg, and in 1823 he received the degree of Doctor of Medicine. L. Gmelin became interested in him, and it was largely due to Gmelin's

[1] See Kopp's Geschichte der Chemie, 4, 440.

influence that Wöhler gave up his intention of practicing medicine and concluded to devote himself entirely to chemistry. For further instruction in his chosen science, Wöhler went to Stockholm to receive instruction from Berzelius, in whose laboratory he continued to work from the fall of 1823 until the middle of the following year. Only a few years since, in a communication entitled "Jugenderinnerungen eines Chemikers," he gave a fascinating account of his journey to Stockholm and his experiences while working with Berzelius. On his return to Germany he was called to teach chemistry in the recently founded municipal trade school (Gewerbschule) at Berlin. He accepted the call, and remained in Berlin until 1832, when he went to Cassel to live. In a short time he was called upon to take part in the direction of the higher trade school at Cassel. He continued to teach and work in Cassel until 1836, when he was appointed professor of chemistry in Göttingen. This office he held at the time of his death, September 23, 1882.

In 1825 Wöhler became acquainted with Liebig, and an intimate friendship resulted, which continued until the death of Liebig, a few years ago. Though they lived far apart, they met during the vacations at their homes, or travelled together. Many important investigations were conceived by them as they talked over the problems of chemistry, and many papers appeared under both their names, containing the results of their joint work. Among such papers may be mentioned: "On Cyanic Acid" (1830); "On Mellithic Acid" (1830); "On Sulphotartaric Acid" (1831); "On Oil of Bitter Almonds, Benzoic Acid and Related Compounds" (1832); "On the Formation of Oil of Bitter Almonds from Amygdalin" (1837); and "On Uric Acid" (1837).

Of the papers included in the above list, the two which most attract attention are those "On the Oil of Bitter Almonds" and "On Uric Acid." In the former it was shown for the first time that in analogous carbon compounds there are groups which remain unchanged, though the compounds containing them may, in other respects, undergo a variety of changes. This is the conception of radicles or residues as we use it at the present day. It cannot be denied that this conception has done very much to simplify the study of organic compounds. The full value of the discovery was recognized at once by Berzelius, who, in a letter to the authors of the paper, proposed that they should call their radicle proin or orthrin (the dawn of day), for the reason that the assumption of its existence might be likened to the dawn of a new day in chemistry. The study of this paper should form a part of the work of every advanced student of chemistry. It is a model of all that is desirable

in a scientific memoir. The paper on Uric Acid is remarkable for the number of interesting transformation products described in it, and the skill displayed in devising methods for the isolation and purification of the new compounds. Comparatively little has been added to our knowledge of uric acid since the appearance of the paper of Liebig and Wöhler.

It would lead too far to attempt to give a complete list of the papers which have appeared under the name of Wöhler alone. In 1828 he made the remarkable discovery that when an aqueous solution of ammonium cyanate, $CNONH_4$, is evaporated, the salt is completely transformed into urea, which has the same percentage composition. It would be difficult to exaggerate the importance of this discovery. That a substance like urea which up to that time had only been met with as a product of processes which take place in the animal body, should be formed in the laboratory out of inorganic compounds, appeared to chemists then to be little less than a miracle. To-day such facts are among the commonest of chemistry. The many brilliant syntheses of well-known and valuable organic compounds which have been made during the past twenty years are results of this discovery of Wöhler.

In 1823 he published a paper on secretion, in the urine, of substances which are foreign to the animal organism, but which are brought into the body. He discovered the transformation of neutral organic salts into carbonates by the process of assimilation.

In 1832 he investigated the dimorphism of arsenious acid and antimony oxide. In 1841 he made the discovery that dimorphous bodies have different fusing points according as they are in the crystallized or amorphous condition.

Among the more remarkable of his investigations in inorganic chemistry are those on methods for the preparation of potassium (1823); on tungsten compounds (1824); the preparation of aluminium (1827); of glucinum and yttrium (1828). In 1856, working with St. Claire Deville, he discovered crystallized boron.

Analytical methods were improved in many ways, and excellent new methods were introduced by him. Further, he did a great deal for the improvement of the processes of applied chemistry.

With Liebig he was associated in editing the "Annalen der Chemie und Pharmacie," and the "Handwörterbuch der Chemie." He wrote a remarkably useful and popular "Grundriss der Chemie." The part relating to inorganic chemistry appeared first in 1831, and was in use until a few years ago, when Fittig wrote his "Grundriss" on the same plan, a work which supplanted its prototype.

The above will serve to give some idea of the great activity of Wöhler's life and the fruitfulness of his labors. While thus contributing largely by his own work directly to the growth of chemistry, he did perhaps as much in the capacity of teacher. Many of the active chemists of the present day have enjoyed the advantages of Wöhler's instruction, and many can trace their success to the impulse gathered in the laboratory at Göttingen. The hand of the old master appears in investigations carried on to-day by his pupils.

Wöhler's was not a speculative mind. He took very little part in the many important discussions on chemical theories which engaged the attention of such men as Dumas, Gerhardt, Berzelius, and Liebig, during the active period of his life. He preferred to deal with the facts as such: and no one ever dealt with the facts of chemistry more successfully. He had a genius for methods which has never been equalled. The obstacles which had baffled his predecessors were surmounted by him with ease. He was in this respect a truly great man.

Personally, Wöhler was modest and retiring. His life was simple and unostentatious. He had a kindly disposition which endeared him to his students, to which fact many American chemists who were students at Göttingen during the time of Wöhler's activity can cordially testify. In short, it may be said deliberately that Wöhler, as a chemist and as a man, was a fit model for all of us and for those who will come after us. Though he is gone, his methods live in every laboratory. His spirit reigns in many: could it reign in all, the chemical world would be the better for it.

I. R.

REVIEWS AND REPORTS.

Analytical Chemistry.

Determination of the Flashing Point of Petroleum.—Engler and Haas[1] have thoroughly tested the different forms of apparatus now in use for the determination of the flashing point of petroleum, and find that all those are worthless in which the determination is made indirectly by measuring the tension of the vapor; because the tension of the vapor of petroleum and its inflammability stand in no simple relations to one another. Under this head are classed the apparatus of Salleron-Urbain, van der Weyde, Mensel and others. Those testers in which the petroleum is heated in an open vessel were also found to give unreliable results. The Saybolt tester used in the United States is constructed on this principle, and gave results that were too high. Among the large number of petroleum testers in which the oil is heated in closed vessels many were found to be constructed on false principles, and they discarded such instruments as Tagliabue's, Sintenis's pyrometer, and Parrish's naphtometer. They further state that the following principles are to be kept in mind in testing petroleum, or in judging of the efficiency of the testing apparatus:

The quantity of petroleum used in each case must be the same, and for each separate test a fresh portion must be taken. The heating must be uniform and slow, and the heating period should extend over 10°; and those oils whose flashing point is but little above the temperature of the air should be cooled about 10° before heating. The intensity of the ignition flame and its distance from the surface of the oil must be the same in all the tests. If the size of this flame be increased and its distance from the oil be diminished, the flashing point will be lowered. The ignition flame must never be so near the oil as to cause local vaporization, and for this reason its time of action should be reduced to a minimum. And in general the conditions for the formation of combustible gases in the testing apparatus should resemble, as nearly as possible, those which occur in lamps or petroleum stoves.

Victor Meyer's method was found to possess the advantages claimed by its author. It consists in bringing 40 cc. of the oil to be tested into a glass cylinder of 200 cc. capacity. The closed cylinder is immersed in a water-bath until the water is nearly on a level with its upper edge, the bath is then heated to the temperature at which it is desired to test the oil. The cylinder is taken

[1] Zeitschrift für analytische Chemie, 20, 1.

from the bath and shaken violently, opened, and a small gas jet brought to its mouth. The temperature at which the oil takes fire is called by Meyer "the true or absolute flashing point," because it is independent of the shape and dimensions of the vessel, of the quantity of the oil taken, and of the distance of the ignition flame from the surface of the oil. The correctness of Meyer's view has also been shown by the experiments of Hörler.[1]

Abel's petroleum tester, adopted by parliamentary act in England, and recently by the German government, was also examined by the authors. The apparatus consists of a small cylindrical petroleum holder provided with a thermometer, and an ingenious device by means of which, on opening the lid of the vessel, the flame of a small lamp is introduced into the opening.[2] The oil holder is surrounded by an air-bath, which in turn is enclosed by a water-bath, the object of the arrangement being to ensure a slow heating of the oil. As the temperature of the oil is thus gradually increased, it is only necessary to slide back the lid from time to time and read the thermometer when the vapor takes fire. Engler and Haas obtained concordant results with this apparatus, but regard the values thus found as too low. The same may be said of Bernstein's tester, except that, in this case, the values were too high.

The best results, however, were obtained with instruments made by the authors themselves, and provided with arrangements for exploding the vapor by means of an electric spark. Engler's apparatus is an improved form of Parrish's naphtometer; while Haas has adopted a modification of Victor Meyer's method. Both instruments are complicated, and considerable skill is required in testing with them.

Skalweit[3] has suggested that the specific gravity, the boiling point, and the index of refraction of petroleum be used in judging of its fitness for use. He finds those oils which give off inflammable vapors to have a specific gravity less than .800, while good petroleum is considerably heavier (.824), and, in the same way, the boiling point and the index of refraction increase as the temperature of the flashing point rises.

Engler and Haas[4] have tested a large number of oils in the ways suggested by Skalweit, and arrived at the conclusion that neither the index of refraction, the boiling point, nor the specific gravity can be used as an accurate means of distinguishing between high and low grades of oils.

Recently Liebermann[5] has invented a new petroleum testing apparatus. The principle adopted is a modification of Victor Meyer's, and consists in forcing a current of air through the heated petroleum. The air becomes charged with the petroleum vapor, and is tested from time to time with a lighted match. That

[1] Dingler's polyt. Journal, **234**, 52. [2] Dingler's polyt. Journal, **245**, 165.
[3] Chemical News, **43**, 77. [4] Zeitschrift für analytische Chemie, **20**, 362.
[5] Zeitschrift für analytische Chemie, **21**, 1.

temperature of the oil at which the current of air ignites is taken as the flashing point.

Detection and Estimation of Fusel Oil.—Until quite recently we have had no accurate method for the determination of fusel oil in alcohol or brandy. In 1837 Meurer suggested a solution of one part of silver nitrate in nine parts of water as a reagent for its detection, stating that when added to alcohol containing fusel oil a reddish brown color is produced, and in case large quantities are present a dark brown precipitate is formed. It was soon found, however, that other substances than amyl alcohol produce brown colored solutions with silver nitrate; and Bouvier[1] observed that on adding potassium iodide to alcohol containing fusel oil the solution is colored yellow, from the decomposition of the iodide. Subsequently Böttger[2] proved that potassium iodide is not decomposed by pure amyl alcohol, and that the decomposition is due to the presence of acids contained in fusel oil. More accurate results are obtained by using a very dilute solution of potassium permanganate, which is decomposed by amyl alcohol much more rapidly than by ethyl alcohol.

Dupré[3] determines fusel oil by oxidizing a definite quantity of the alcohol in a closed vessel with potassium bichromate and sulphuric acid. After removal of excess of the oxidizing reagents, the organic acids are distilled, and, by repeated fractional distillation, the acetic acid is separated as completely as possible. The remaining acids are saturated with barium hydroxide, and the salts analyzed; a difference between the percentage of barium found and that of barium in barium acetate proves the presence of fusel oil, and the amount of difference gives some idea of its quantity. Betelli[4] dilutes 5 cc. of the alcohol to be tested with 6–7 volumes of water, and adds 15–20 drops of chloroform and shakes thoroughly. If fusel oil is present its odor may be detected by evaporating the chloroform; or, by treatment with sulphuric acid and sodium acetate, the ether is obtained, which can be readily recognized. Jorissen[5] tests for fusel oil by adding 10 drops of colorless aniline and 2–3 drops of hydrochloric acid to 10 cc. of the alcohol. In the presence of fusel oil a red color is produced within a short time, which can be detected when not more than .1 per cent. is present. But Foerster[6] objects to this method because he finds the color to be due to the presence of furfurol, and that pure amyl alcohol gives no color with aniline and hydrochloric acid.

Hager[7] detects fusel oil as follows: If the spirit contains more than 60 per cent. of alcohol it is diluted with an equal volume of water and some glycerine added, pieces of filter paper are then saturated with the liquid and exposed to the air. After the

[1] Zeitschrift f. anal. Chem. **11**, 343.
[2] Dingler's polytech. Journ. **207**, 516.
[3] Pharm. J. Trans. [3] **6**, 867.
[4] Berichte d. deutschen chem. Gesellsch. **8**, 72.
[5] Pharm. Centralhalle **22**, 3.
[6] Berichte d. deutsch. chem. Gesellsch. **15**, 230.
[7] Pharm. Centralhalle **22**, 236.

evaporation of the alcohol, the odor of the fusel oil can be readily detected. For the quantitative determination he distills 100 cc. of the alcohol in a flask of 150–200 cc. capacity connected with a condenser, and so arranged that the apparatus does not extend more than 20 cm. above the water-bath. This arrangement prevents the fusel oil from passing over. If the alcohol is stronger than 70 per cent. and the height of the distillation apparatus is not more than 17 cm., the residue in the flask may be weighed as fusel oil. With a weaker alcohol, or an apparatus which projects further out of the water-bath, the residual fusel oil is mixed with water. It can, however, be separated by adding strong alcohol and redistilling, or by treating with ether, which dissolves the amyl alcohol, and distilling, the temperature being raised finally to 60°.

Marquardt,[1] like Betelli, extracts the fusel oil from alcohol by means of chloroform, and by oxidation converts it into valeric acid. From the quantity of barium valerate found he calculates the amount of amyl alcohol present in the original solution. 150 cc. of the spirit, which has been diluted so as to contain 12–15 per cent. of alcohol, are shaken up thoroughly with 50 cc. of chloroform, the aqueous layer drawn off and shaken with a fresh portion of chloroform. This treatment is repeated several times. The extracts are then united and washed repeatedly with water. The chloroform, which is now free from alcohol and contains all the fusel oil, is treated with a solution of 5 grams of potassium bichromate in 30 grams of water and 2 grams of sulphuric acid, and then heated in a closed flask for six hours on a water-bath at 85°. The contents of the flask are then distilled, the distillate saturated with barium carbonate, and the chloroform distilled; the residue is evaporated to a small volume, the excess of barium carbonate filtered off, and the filtrate evaporated to dryness, and weighed. The residue is dissolved in water, a few drops of nitric acid added, and the solution divided into two portions. In the first portion the barium is determined; in the second the barium chloride. The total per cent. of barium minus that of barium chloride gives the amount present as barium valerate, from which is calculated the per cent. of amyl alcohol. By this process the author has determined one part of fusel oil in ten thousand of alcohol. To detect very minute quantities of fusel oil, the chloroform extracts are treated with several drops of sulphuric acid and enough potassium permanganate to keep the solution red for twenty-four hours. If allowed to stand in a test tube, the odor of valeric aldehyde will first be noticed, then that of amyl valerate, and lastly that of valeric acid.

Pure Grape Sugar and its Estimation with Standard Solutions.—Worm Müller[2] finds that, contrary to the statements of Soxhlet, grape sugar can be crystallized from its solution in abso-

[1] Berichte d. deutsch. chem. Gesellsch. **15**, 1370 and 1663. [2] Journ. f. prakt. Chem. **26**, 78.

lute alcohol in a perfectly pure and anhydrous condition. Otto[1] states that the most advantageous conditions for its preparation are as follows: 600 cc. of 80 per cent. alcohol, to which 20 cc. of concentrated hydrochloric acid have been added, are treated with cane sugar, from time to time, until in about three or four weeks the solution will have become saturated. It is now filtered into a dry flask through a paper previously moistened with alcohol, and the filtered solution set aside in a cool place to allow the grape sugar to crystallize. In about four or five weeks the separation will be complete; the liquid is then decanted, and 90 per cent. alcohol added to the crystals. After standing twenty-four hours, the mass is stirred up well and the solution filtered with the aid of a pump. The crystals are then pulverized under absolute alcohol, and, after standing some time, are again filtered. This process of purification is repeated until the filtrate gives no acid reaction, and a concentrated solution of the sugar gives no precipitate with nitric acid and silver nitrate. The sugar is then dried, first in a vacuum, then over sulphuric acid, and lastly, before using, it is dried in a water-bath, the temperature of which is gradually raised from 40° to 100°, to avoid the fusion which takes place if the sugar be immediately introduced into the bath at 100°. Prepared in this way the sugar is perfectly pure, and it is unnecessary to recrystallize from absolute alcohol.

When grape sugar is titrated with Knapp's solution (10 grams $Hg(CN)_2$ and 100 cc. NaOH (sp. gr. 1.145) to the litre), Otto finds it necessary to dilute the latter with from two to three volumes of water, and to add the sugar solution (which should contain less than 1 per cent.) in small quantities (2 cc.) at a time, boiling after each addition. It is only by observing these precautions that he obtained concordant results. The end of the reaction was ascertained by testing a drop of the solution with ammonium sulphide.

Degener[2] ascribes the varying reducing power of Fehling's solution to the easily reducible copper compound which it contains. He dissolves copper tartrate in sodium hydroxide (3 molecules $CuC_4H_4O_6$ to 4NaOH) and adds the usual quantity of sodium potassium tartrate and sodium hydroxide required to make Fehling's solution. Prepared in this way, he regards the copper as being present in a different form from that in Fehling's solution; and states that whenever 3–4 molecules of free alkali and 16–18 molecules of sodium potassium tartrate are present to 3 atoms of copper, the degree of concentration of the solution has no effect upon its reducing power; and that, after boiling, the sugar will have reduced copper in the proportion of six molecules of copper oxide to one of sugar.

E. H. K.

[1] Journ. f. prakt. Chem. **26**, 87.
[2] Zeitschrift d. Vereins f. Rübenindustrie, 1881, 349.

Carbonic Acid in the Air.

Owing to the varied and important functions of carbonic acid in our atmosphere, the investigation of its amount in the air has always been an attractive problem to chemists. Ever since it has been known that animals produce carbonic acid by respiration, and that plants consume it, appropriating carbon and liberating oxygen, the question has often been asked, Do these two great processes compensate each other perfectly, or is there a tendency towards increase or decrease in the amount of this atmospheric constituent?

The chief causes of production of the gas are:

1. The respiration of animals.
2. Combustion of carbonized material.
3. Exhalations of carbonic acid caused by volcanoes and other intra-terrestrial agencies.

The causes of consumption are chiefly:

1. The decomposition of carbonic acid by plant life.
2. The formation of carbonate of lime by the absorption of atmospheric carbonic acid through the agency of certain animalculae, giving rise to coral reefs and islands and vast limestone deposits.

Owing to insufficient data it cannot be said whether atmospheric carbonic acid is increasing or decreasing; but certainly, if any essential change is going on, such change must be extremely slow, and the most accurate and systematic analyses carried on for years would be necessary to reveal it. From such knowledge as we have, however, the *total* amount of this gas in the atmosphere seems to be constant. In the text-books of to-day we find usually something like the following statement: The atmosphere contains a small amount of carbonic acid, varying usually between 4 and 6 parts by volume per 10,000 of air. Within the last few years a number of investigators have applied themselves in the most painstaking manner to ascertaining what is the correct *mean* proportion of carbonic acid in the air, and what are the limits of variation in the amount of this gas. According as the methods for determining carbonic acid in the air have become more perfect, it is noticeable that the proportion has been found to be less and less, until now, in the light of a number of independent investigations, the analytical processes involved in which were tested and retested until it seems impossible to raise a reasonable doubt as to their reliability, we have as the mean proportion 29.62 parts by volume of carbonic acid to 100,000 of air. For the limits of variation we have the figures 27.00 to about 35.00 parts per 100,000. (These figures are taken from M. Reiset's tables referred to further on.)

A very natural question may now be asked, namely, to what cause or causes is this variation in the proportion of carbonic acid due? *A priori* we would expect to find more carbonic acid in the atmosphere surrounding an abundant source of this gas, for ex-

ample a large city, than in the atmosphere of the open country, where not only is the production of the gas comparatively small, but where also the decomposing action of vegetation is naturally more active. We would expect to find less carbonic acid in the air surrounding abundant vegetation than in that covering a desert devoid of plant life. Questions to which the answers cannot so readily be anticipated also arise, for example: For a given place is there more or less carbonic acid in the air on a clear day than on a cloudy day? Is there a difference in the proportion between day and night, or between winter and summer? Is there more or less carbonic acid at the bottom of a mountain than at the top? Is there more or less in the air near the sea than in that of inland country? etc.

The number of investigators who have endeavored to solve questions relative to the variation in the proportion of atmospheric carbonic acid is large; few of them, however, have succeeded in furnishing experimental evidence so definite and convincing in character as that submitted to the scientific world by M. J. Reiset[1] in answer to problems of the nature given above. Appreciating the delicate nature of the task before him, M. Reiset's first efforts were directed to securing an analytical method sufficiently accurate to reveal the minutest variations in the small proportion of the gas under consideration. The principle involved in his method is the precipitation of carbonate of barium by passing a known volume of air through a solution of baryta, the strength of which is determined before and after the operation by means of sulphuric acid of known strength. The precautions taken to avoid every imaginable source of error are such as to give entire confidence in the results obtained. The number of determinations made by Reiset is 283, each determination requiring from seven to twelve hours' time for the passage of about 600 litres of air through the absorbing liquid. Some of the determinations lasted twenty-three or twenty-four hours, in order to obtain the mean proportion directly.

The following observations were also made in connection with each analysis:

Hour and minute of beginning, day or night.

Duration of analysis.

Weight of air dry at 0° C. and 760 mm. in the aspirator.

Weight of atmospheric aqueous vapor in air analyzed.

Temperature of the air, and pressure.

Direction of the wind and state of the atmosphere.

By an examination of the tables compiled by M. Reiset the following results are revealed:

1. The maxima in the proportion of carbonic acid always correspond to cloudy, foggy or misty weather.

[1] Annales de Chimie et de Physique, June, 1882.

2. Air collected during the night contains more carbonic acid than that collected during the day.

3. Minima correspond to days of fine weather, with bright sunlight and absence of clouds.

To determine the influence of vegetation, comparative and simultaneous observations were made at two different stations, one in the midst of abundant plant growth, the other in an open field. The diffusion of the gas in the air is, however, so rapid that variations in its amount due to vegetation are scarcely appreciable. Air analyzed in a fine field of red clover, in the month of June, gave a mean of 28.98 per 100,000; simultaneous observations at the normal station gave in the mean 29.15. The mean of analysis in a rich field of barley was 28.29 per 100,000; that at the normal station 29.33. The following incidental and interesting item was brought out during a single determination: The presence of a flock of three hundred sheep near the apparatus on a certain day of fine weather caused a notable increase in the proportion of carbonic acid; the figures obtained were 31.78 per 100,000. A number of analyses were made near the park Monceau in Paris. During the month of May, when fires begin to be extinguished, the mean was found to be 30.57 per 100,000 of air. The maximum, 35.16, was obtained on the 27th of January, 1879, during the period of most active combustion; the minimum, 29.13, was obtained May 31, 1875. The normal variations in the proportion of carbonic acid are generally between 28 and 30 per 100,000 of air. These variations are more sudden and more numerous during the summer.

Let us now turn our attention to the labors of MM. Müntz and Aubin.[1] These investigators commenced their work with the purpose of solving the three following problems, viz:

1. To determine whether the proportions $\frac{1}{10000}$ and $\frac{1}{10000}$ found by the ealier investigators are not too high as indicated by certain more modern analyses?

2. Does the proportion of carbonic acid in the air vary between wide limits, or is it not practically constant?

3. Is there or not a considerable difference in the proportion for different strata of the atmosphere?

The method employed for the answering of these questions consists briefly in passing a known volume of air through tubes containing pumice-stone saturated with a solution of caustic potash, and, after the operation, in liberating the carbonic acid by means of sulphuric acid and measuring the volume of the gas directly. This process has the following advantage: Tubes may be prepared, filled with the pumice-stone, sealed at both ends, transported to the spot at which the air is to be analyzed, and, after passing the desired amount of air through them, again sealed, returned to the laboratory (after an indefinite time), where the determination of the gas can be made. The delicate part of the operation is thus

[1] Annales de Chimie et de Physique, June, 1882.

performed where there are laboratory facilities. Another advantage consists in the rapidity with which the air can safely be passed through these tubes, *i. e.* at the rate of 3 litres per minute. Before adopting this method the authors first tested it thoroughly by operating on air first deprived of carbonic acid and then mixed with a small but known amount of the gas, which was then redetermined; thus in an artificial air containing 3.03 CO_2 per 10,000 air, 2.98 was found. A large number of test experiments were made before the method was finally adopted.

For the investigation of the lower atmospheric strata Müntz and Aubin established two stations, one at Paris at the Conservatoire des Arts et Métiers, 6m. above the ground, the other in the open plain which extends towards the plateau de Gravelle 4m. above the ground. The mean proportion found for the Paris station is 3.19 parts by volume of carbonic acid to 10,000 of air; the mean for the country station is 2.84. These figures do not differ materially from those given by M. Reiset.

A number of comparative determinations were made at Paris and Joinville. For Paris we have the figures 2.99, 3.06, 2.89, 2.96; for Joinville the figures 2.74, 2.72, 2.85, 2.79. It is thus established that the air of Paris contains more carbonic acid than that of the country.

An examination of the tables submitted by Müntz and Aubin shows that the proportion is at its minimum when the air is disturbed and the sky clear; at its maximum when the weather is cloudy and calm. The absolute minimum is 2.70, the absolute maximum 3.17. These figures confirm those of M. Reiset.

Having thus arrived at solutions of the first two problems, the influence of altitude was investigated. Much discussion has taken place on this point, some observers having found the proportion greater at high than at low altitudes, others greater at low than at high elevations.

The summit of the Pic du Midi, altitude 2877 m., in the Pyrenees was selected for high altitude observations. The mean of fourteen analyses at the summit is 2.86; that for low altitude observations was 2.81; hence the proportion is not sensibly different in the upper strata of the air.

Before closing it will perhaps not be out of place to state certain results arrived at by M. Schloesing,[1] who has a theory that the sea is a great regulator of the proportion of atmospheric carbonic acid. This investigator found that certain neutral carbonates of the alkaline earths placed with water in an atmosphere containing carbonic acid are able to absorb this gas and thus to pass into solution as bicarbonates. The extent of this action is a function of the tension of the gas, and when the tension is sufficiently low the bicarbonates give up carbonic acid and are reprecipitated as neutral carbonates. His theory is then that the sea, by absorb-

[1] Comptes Rendus, **90**, 1410.

ing or emitting carbonic acid according to the tension of the latter in the air, acts as a reservoir or regulator for this atmospheric constituent.

Want of space only prevents a consideration of the investigations of many other observers whose labors are of interest in connection with the subject. We may now not only consider ourselves as in possession of figures expressing very accurately the general mean proportion of carbonic acid in the air, but also as having some reliable knowledge of causes of local variation.

Another question which might well be asked is this: Is there not some connection between the variations in the proportion of carbonic acid in the air and the great general movements of the latter? This question has been propounded and a solution attempted by M. Marie-Davy, but since the method employed and the analytical results obtained by him have been rather severely criticized, the question must still be considered an open one. Moreover, definite knowledge on this point can be gained only by a long series of simultaneous determinations at places widely separated. For this purpose the method of Müntz and Aubin seems eminently well adapted, since skilled manipulation in connection with it is essential only in the laboratory, where the necessary tubes might be prepared, sent to various stations, and, after passing the necessary amount of air through them, returned to the laboratory for the completion of the analysis. W. C. D.

On Some Recent Improvements in Industrial Chemical Processes.[1]

The improvements in question relate to the manufacture of chlorates, to the manufacture of carbonate of potash, to the recovery of sulphur from alkali waste, and to the industries of sulphuric acid, sulphate of soda, and chlorine.

Commencing with the chlorates, I may remind you that the manufacture of these salts is based on the reactions which take place when milk of lime is treated by an excess of chlorine. Theoretically, the product of the treatment of milk of lime by chlorine should be a mixed solution of one equivalent of calcium chlorate and five equivalents of calcium chloride:

$$6CaO+12Cl=CaCl_2O_6+5CaCl_2.$$

In industrial practice, however, the product always contains appreciably more than five equivalents of calcium chloride. It never contains less than five and a half equivalents, and frequently con-

[1] This paper was recently read by Mr. Walter Weldon before the "Society of Chemical Industry," and has appeared in the Journal of the Society.

tains as much as six and a half equivalents, of that salt. Its average composition may be taken to be

$$CaCl_2O_6 + 6CaCl_2.$$

Between calcium chlorate, in solution in water, and potassium chloride, double decomposition takes place; and it is by this double decomposition that chlorate of potash is now invariably manufactured. Continental manufacturers usually treat simply milk of lime by chlorine, and then add potassium chloride to the resulting "crude chlorate liquor," as it is called, whilst English manufacturers usually add their potassium chloride to their milk of lime before commencing the treatment by chlorine; but in both cases equally the final product is a mixed solution of two of potassium chlorate and from six and a half to seven and a half, say on an average seven, of calcium chloride:

$$CaCl_2O_6 + 6CaCl_2 + 2KCl = 2KClO_3 + 7CaCl_2.$$

This mixed solution is treated for the separation of potassium chlorate from it by being concentrated to a certain point by evaporation and then allowed to cool, when chlorate of potash crystallizes out. The whole of the potassium chlorate, however, does not crystallize out; from fourteen or fifteen to as much as twenty-five per cent. of it, according to circumstances, remains with the mother-liquor. By further evaporating the mother-liquor, and then again cooling, more chlorate of potash would be obtained; but this further quantity would be so contaminated by calcium chloride, which would crystallize out with it, as to be inapplicable to any of the purposes for which chlorate of potash is at present required. The mother-liquor is therefore usually thrown away. Attempts have from time to time been made to turn it to some small account by treating it by hydrochloric acid, from which the potassium chlorate in it then liberates chlorine; but this operation is attended by a certain amount of danger, and moreover chlorine is now produced so cheaply in other ways that the game is not worth the candle.

In the manufacture of chlorate of potash, then, as at present ordinarily conducted, there is a loss of from fifteen to twenty-five per cent. of the total chlorate produced. The improvement to which I shall first invite your attention enables this loss to be reduced to below five per cent. The improvement in question was devised, however, not for the purpose of thus diminishing the loss in the manufacture of chlorate of potash, but for quite another purpose, and its application to this other purpose may most conveniently be noticed first.

The members present will be aware that, although until comparatively recently, the only chlorate which occurred in commerce in any considerable quantity was the chlorate of potash, within the last few years a demand has sprung up for the very much more

soluble salt, chlorate of soda. This demand for chlorate of soda, I may say, in passing, is an outcome of our President, Professor Roscoe's famous researches on vanadium. Some of the rougher furnace work on the raw material from which Professor Roscoe obtained his vanadium was done for him by Mr. Samuel Mellor, of the Magnesium Metal Company, at that company's works at Patricroft, near Manchester. In acknowledgment of it, Professor Roscoe presented to Mr. Mellor some ounces of vanadium salts, and Mr. Mellor sent them to Messrs. Johnson and Matthey, for whom some portions of them were obtained by the late Mr. John Lightfoot, of Accrington, and by Mr. Robert Pinkney, of London. Both these gentlemen experimented with them in connection with their application to the production of aniline black, with the result of finding that they were far more effective for the purpose than the copper salts which had previously been used, while their use instead of copper salts would avoid the inconveniences which had led to the abandonment of the use of aniline black by many firms of calico-printers, that inconvenience being that when using a "color" containing a copper salt, copper deposited on the "doctors," or scrapers. Before knowing of these results, Dr. Roscoe had urged Mr. Mellor to try to find a deposit of vanadium, and to commence the manufacture of vanadium salts, his view being that if compounds possessing such remarkable properties were only rendered accessible to chemists, uses would speedily be found for them. Mr. Mellor acted on this advice, and, after surmounting very great difficulties, was at length enabled to put vanadium salts into the market. To induce calico-printers to use them, however, was no easy task. It took immense labor to convince them that a vanadium salt at twenty-one shillings an ounce could be cheaper for their purpose than copper sulphide at a few pence per pound, which it, however, certainly is, since only one halfpennyworth of the costly vanadium salt is required for each gallon of "color," whereas, when using copper sulphide, the quantity of it required per gallon of "color" costs at least seven halfpence. There was, moreover, a further difficulty. The "color" used for printing aniline black must contain, not only an aniline salt and a metallic salt, but also an oxidizing agent; and the only available oxidizing agent then occurring in commerce was chlorate of potash. But the solubility of chlorate of potash is comparatively so slight that only four ounces of it could be got dissolved in each gallon of "color," and this was insufficient to completely oxidize the aniline, and the blacks produced were therefore apt to turn green. Before aniline black could be largely employed by calico-printers, even now that vanadium salts were at their disposal, it was therefore necessary to provide them with a more soluble oxidizing agent than chlorate of potash; and Mr. Mellor was thus led to undertake the manufacture of chlorate of soda. Some calico-printers had already begun to use chlorate of soda, producing it themselves, in solution, by various double decompositions with chlorate of potash; but Mr. Mellor was

the first to produce chlorate of soda in crystals, and to render it readily obtainable by whosoever required it; and it is to his introduction into commerce of that salt, together with vanadium salts, that the great extension which the application of aniline black in calico printing has since undergone is mainly due. Chlorate of soda, so far as I am aware, is at present used only by calico-printers, and only in the printing of aniline black; but some two hundred tons of it are now produced per annum, and its manufacture is still extending.

For some years after a demand for chlorate of soda was thus created by Mr. Mellor, the demand for that salt was met by various methods, all of which had this in common, that previously manufactured chlorate of potash was taken as their starting-point. Of these methods it will be sufficient to mention that which consisted in decomposing chlorate of potash by aqueous hydrofluosilicic acid, thus obtaining silicofluoride of potassium and a solution of chloric acid, and then saturating the latter either by caustic soda or by sodium carbonate.

The reason why such methods as these were resorted to appears to have lain in the very positive statement of the books that sodium chlorate cannot be separated from a mixed solution of sodium chlorate and sodium chloride, by reason of the two salts being of equal solubility. This statement appeared to render hopeless any attempt to manufacture sodium chlorate by means of the otherwise obvious reaction of sodium sulphate on "crude chlorate liquor," since that reaction would yield a mixed solution of sodium chlorate and sodium chloride, containing very much more of the latter salt than of the former:

$$CaCl_2O_6 + 5.5CaCl_2 + 6.5Na_2SO_4 = 2NaClO_3 + 11NaCl + 6.5CaSO_4$$

One chemist, however, declined to accept this statement of the books. My friend, Monsieur Pechiney, of the great chemical works of Salindres, in the south of France, preferred to investigate the solubility of sodium chlorate for himself; and he found that the statement of the books that its solubility is almost exactly the same as that of sodium chloride is true only for certain temperatures. At ordinary temperatures the solubility of sodium chlorate is almost the same as that of sodium chloride; but at higher than ordinary temperatures the respective solubilities of the two salts are widely different. While the solubility of sodium chloride, as we know, does not appreciably increase with increase of temperature, M. Pechiney found, not only that the solubility of sodium chlorate does increase with increase of temperature, but that it increases to such an extent that mere concentration by evaporation of a mixed solution of sodium chlorate and sodium chloride will cause practically the whole of the sodium chloride to fall down, or "salt out," leaving sodium chlorate only in solution.

Having obtained this result, M. Pechiney was enabled some four year ago to commence producing chlorate of soda by the following series of operations:

1. Production of crude chlorate liquor, by acting upon milk of lime by excess of chlorine.
2. Treatment of the crude chlorate liquor by sodium sulphate.
3. Filtration of the product of the second operation by means of the centrifugal hydro-extractor.
4. Evaporation of the filtrate until sodium chloride ceased to fall, the sodium chloride being constantly "fished out" as it fell.
5. Cooling of the solution thus freed from sodium chloride, giving crystals of practically pure chlorate of soda, and a small quantity of mother-liquor consisting of a saturated solution of that salt.

While, however, this method of manufacturing chlorate of soda was a very great advance upon all preceding methods, M. Pechiney was by no means satisfied with it. As is shown by the equation given above, the reaction of sodium sulphate on crude chlorate liquor requires at least six and a half of Na_2SO_4 to give two of $NaClO_3$, and its products are a mixed solution of two of sodium chlorate and at least eleven of sodium chloride, holding in suspension at least six and a half of calcium sulphate. The presence in the product of so much calcium sulphate occasioned considerable loss of sodium chlorate, since it was impossible industrially to separate the calcium sulphate completely from the mixed solution without incurring too much expense for the evaporation of wash-waters; and the presence of so large a proportion of sodium chloride in the mixed solution was a further cause of loss of chlorate, since in fishing out the sodium chloride, during the evaporation of the filtrate from the calcium sulphate, much adherent solution of sodium chlorate was of course necessarily fished out with it. Moreover, water enough had to be used to hold in solution not only the two of sodium chlorate, but also the eleven of sodium chloride; and all this water, or at least all of it not lost as mother-liquor adherent to the solid impurities which had to be separated from the sodium chlorate, as well as the water used for washing the calcium sulphate, had, of course, to be afterwards driven off by evaporation. In a district in which coal is dear this was a serious matter.

Now, it is obvious that eleven-thirteenths of the calcium sulphate and the whole of the sodium chloride contained in the product of the reaction of sodium sulphate on crude chlorate liquor are due to the five and a half equivalents of calcium chloride contained in that liquor. Between calcium chlorate only and sodium sulphate the reaction would be—

$$CaCl_2O_6 + Na_2SO_4 = 2NaClO_3 + CaSO_4.$$

This reaction would yield, instead of a mixed solution of two of

sodium chlorate and eleven of sodium chloride, holding in suspension six and a half of calcium sulphate, a solution of two of sodium chlorate with no sodium chloride at all, holding in suspension only one of calcium sulphate. If, therefore, in the manufacture of sodium chlorate, one could start from calcium chlorate exempt from calcium chloride, one would gain some very important advantages. Not only would the consumption of sodium sulphate, per given quantity of sodium chlorate produced, be only two-thirteenths of the quantity required when starting from crude chlorate liquor, while the total quantity of materials to be dealt with, and the quantity of water to be evaporated, would also be less, in about the same proportion, than in the latter case, but the loss of sodium chlorate would be only one-tenth of what it is when starting from crude chlorate liquor, by reason of the amount of foreign bodies to be separated from the sodium chlorate being only one-tenth of the total amount which is present with that salt when it is produced by the reaction of sodium sulphate on calcium chlorate associated with five and a half equivalents of calcium chloride.

These considerations led M. Pechiney to attempt to obtain industrially, under conditions under which it should be available for the production of sodium chlorate from it, if not absolutely pure calcium chlorate, at least a mixture of calcium chlorate and calcium chloride containing a very much smaller proportion of the latter salt than is contained in the crude product of the action of chlorine on milk of lime. It being hopeless to obtain calcium chlorate by any new reaction, M. Pechiney proposed to himself the problem of separating calcium chloride from crude chlorate liquor. For my own part, although perhaps not entirely lacking boldness in such matters, I must say that if this problem had been proposed to me, I should have recoiled before it, and should have regarded its solution as impracticable. M. Pechiney, however, zealously aided by his friend and mine, M. Gladyzc, the very able chemist attached to the works of Salindres, has solved it in a very simple way.

The crude chlorate liquor produced at Salindres contains five and a half equivalents of calcium chloride, and has a density of 25° Beaumé. M. Pechiney now evaporates that liquor until its density while boiling is 48° Beaumé. He then cools the liquor so concentrated to at least 12° C., but not below 10° C. Of its five and a half equivalents of calcium chloride, 4.3 equivalents are thus caused to crystallize out as $CaCl_2.2H_2O$. The concentrated liquor must be cooled to at least 12° C., or this proportion of calcium chloride would not crystallize out; but it must not be cooled below 10° C. or calcium chlorate would crystallize out as well. The crystals obtained between these limits of temperature have no crystallized calcium chlorate with them, and they are of a nature permitting them to be separated from their mother-liquor, by means of the

hydro-extractor, so completely, that the loss of chlorate through mother-liquor adherent to them is barely appreciable. The mother-liquor is a solution of 1.0 equivalent of calcium chlorate and 1.2 equivalent of calcium chloride. To this liquor M. Pechiney now adds, first its own volume of water, and then three times 1.2 equivalents of lime. He then heats to at least 80° C., to determine the formation of calcium oxychloride. He then cools to ordinary temperatures, and then again filters by means of the hydro-extractor. The filtrate obtained this time is a solution of one equivalent of calcium chlorate and only three-tenths of an equivalent of calcium chloride, and thus contains less than one-eighteenth of the proportion of calcium chloride which was contained in the crude chlorate-liquor commenced with. The last three-tenths of an equivalent of calcium chloride M. Pechiney has hitherto failed to separate; but the separation of all but that small proportion is now daily performed at Salindres on a very considerable scale.

I ought here to say that the mixture of calcium oxychloride and excess of lime which is separated by the second filtration is much more retentive of mother-liquor than the crystals of hydrated calcium chloride which are separated by the first filtration; but this occasions no loss of chlorate, because M. Pechiney uses the mixture of calcium oxychloride and free lime for the preparation of more chlorate liquor. And in this connection I may mention an interesting point. While the reaction of chlorine upon milk of lime takes place with evolution of heat, the formation of calcium oxychloride, by the combination of calcium chloride with lime, takes place with an absorption of heat, and the quantity of heat absorbed in the one case seems to be just the same as the quantity evolved in the other. Hence, while the action of chlorine on milk of lime causes a rise of temperature, there is no change of temperature at all when calcium oxychloride is treated by chlorine, the heat liberated by the reaction of the chlorine on the lime of the oxychloride being just sufficient to decompose the oxychloride and no more.

At Salindres, then, there is now regularly produced a solution of calcium chlorate having associated with it only three-tenths of an equivalent of calcium chloride instead of the five and a half of chloride per one of chlorate, which are contained in crude chlorate liquor. I will not further dwell upon the obvious economy with which M. Pechiney is thus enabled to manufacture chlorate of soda; but I may here recur for one moment to chlorate of potash. M. Pechiney now uses in the manufacture of this salt also the solution obtained by separating calcium chloride from crude chlorate liquor, in the manner I have indicated, and he is thus enabled to obtain his potassium chlorate associated with so much less calcium chloride than formerly, that he can regularly crystallize out from his solutions of the two salts fully ninety-five per cent. of the potassium chlorate contained in them, in place of the seventy-five per cent. only, which is all that it is possible to crys-

tallize out in the climate of Salindres from the mixed solution of those two salts produced in the ordinary way.

While by realizing a practical method of separating calcium chloride from calcium chlorate, as contained in crude chlorate liquor, M. Pechiney is able, as we have seen, to effect a very considerable economy in the manufacture of chlorate of soda, and a large, though not equally large, economy in the manufacture of chlorate of potash, the event will probably show that he has done very much more than this. There is every probability that his new product—1.0 of calcium chlorate and 0.3 of calcium chloride—will itself become an article of commerce, and will be largely applied in the arts to other purposes than those to which M. Pechiney himself applies it. Solution of pure calcium chlorate, treated by sulphuric acid, would of course give a solution of chloric acid; while a solution of 1.0 of calcium chlorate and 0.3 of calcium chloride, similarly treated by sulphuric acid, gives a mixed solution of chloric acid and of the products of the reaction of chloric and hydrochloric acids upon each other. Such a solution attacks many organic bodies with remarkable energy, and already promises to give results, in connection with the manufacture of organic coloring matters, of very exceptional interest and importance. I have no doubt, for my own part, that calcium chlorate, now for the first time placed in the hands of the industrial chemist, will be found by him an instrument of extreme utility.

I will next touch very briefly upon two other processes which M. Pechiney has recently introduced into his own works, although they are processes of only limited applicability. One of them is a process for recovering sulphur from soda waste. The works of Salindres are situated in the midst of vineyards, or what were such before the days of the phylloxera, and they are no exception to the rule that in the neighborhood of all inland soda-works vast quantities of "tank-waste" accumulate. From heaps of tank-waste exposed to atmospheric influences, there constantly runs, as we know, little rivulets of "yellow liquor," consisting essentially of a mixed solution of calcium sulphydrate and calcium bisulphide. It is believed by many that such a solution would be a capital thing for vineyards afflicted with phylloxera; but the farmers in M. Pechiney's neighborhood preferred to regard it as an excuse for getting M. Pechiney to pay them damages. In all countries to which my experience extends, I have noticed that farmers have a tendency to prefer to exploit any chemical work in their neighborhood rather than to exploit their land. To get rid of all annoyance from this cause, it was necessary for M. Pechiney to treat his yellow liquor for the recovery of sulphur from it; and he has for some time done this by a process somewhat simpler than any in use elsewhere. He simply injects air into the yellow liquor, by means of a Körting's injector, and then, when oxidation has just reached the point at which treatment of the product by an acid would not cause evolution of either H_2S or SO_2, he decomposes the product by

hydrochloric acid. Apart from its simplicity, and its requiring so little labor and plant, the chief point of interest about this process is that during the operation of oxidising the yellow liquor there occurs a considerable precipitation of lime. The lime is precipitated in a peculiarly dense state (I exhibit a sample of it), permitting it to be separated from the mother-liquor very readily and completely. Owing to this separation of lime during the operation of oxidising the mother-liquor, the quantity of hydrochloric acid required for the decomposition of the oxidised product is very appreciably less, per given quantity of sulphur obtained, than in any other process for obtaining sulphur from alkali waste, excepting one which I shall have to refer to further on, which is at present only in the experimental stage, but which is likely, I think, to come into general use, and in which no acid will be used at all. This precipitation of lime, and of lime only, is of course due to a part of the calcium sulphide, or of one or more of the calcium sulphides, present in the yellow liquor, giving up sulphur in exchange for oxygen, the sulphur thus replaced going to raise the remainder, or some part of the remainder, of the sulphide or sulphides present, to some higher state of sulphurisation.

The company which owns the works of Salindres also owns the great salt-work of Giraud, in that one of the deltas of the Rhone which is known as Camargue. It was at Giraud that was worked out by my friend, the late Henri Merle, the founder both of Giraud and of Salindres, the process, suggested by the late Professor Balard, the discoverer of bromine, for separating potassium chloride and magnesium sulphate from the mother-liquor left after sodium chloride has crystallized out from salt water concentrated by natural evaporation. This process is practiced on a very large scale at Giraud, and at a certain stage of it there is obtained a mixed solution of sodium chloride and magnesium sulphate. This mixed solution is submitted to artificial refrigeration, by means of Carré's machine, when double decomposition takes place, producing crystallized sodium sulphate and solution of magnesium chloride, which are then separated from each other by means of the hydro-extractor. The sodium sulphate so obtained has associated with it ten atoms of water. Coal at Giraud is very dear; and even where coal is cheap the dehydration of hydrated sodium sulphate, by heating it in furnaces, is a somewhat troublesome operation. M. Pechiney was therefore led to seek some better means of dehydrating the vast quantities of hydrated sodium sulphate produced at Giraud, and the method which he finally arrived at, and now uses exclusively, is as follows: He first adds to the hydrated sodium sulphate a certain proportion of "sel mixte," the product so called being the mixture of sodium chloride and magnesium sulphate which is deposited during the concentration of the mother-liquor, by sun-heat, to 35°B., the degree of concentration at which it begins to deposit double chloride of magnesium and potassium. He then charges the mixture so formed into iron cylinders, fur-

nished with steam coils, by means of which the contents of the cylinders can be rapidly heated. When the contents of the cylinders have attained a temperature of about 35°C.—though M. Pechiney really heats to from 70°C. to 80°C., in order that cooling to below 35°C. shall not take place in the succeeding operation—the contents of the cylinders are found to have become a mixture of anhydrous sodium sulphate with a saturated solution of "sel mixte." The "sel mixte" has dissolved in what was the water of hydration of the sodium sulphate, and all the latter has become anhydrous. The anhydrous sulphate is then separated from the solution of "sel mixte" by means of the hydro-extractor. The whole process is performed in a few minutes, and its only cost is for a very small amount of labor and steam. The anhydrous sulphate obtained is the full quantity corresponding to the hydrated sulphate treated, and it is almost chemically pure. The solution filtered from it is employed for the production of more hydrated sulphate.

(*To be continued.*)

Chemical Nomenclature.

With the desire to aid, as far as possible, in securing uniformity in chemical nomenclature, the simple and excellent rules proposed for this purpose by Dr. Henry Watts, the editor of the Journal of the (London) Chemical Society, are here reprinted. It is to be hoped that American writers on chemical subjects will accustom themselves to observe the rules, unless there are good reasons for deviating from them. What *good* reasons can be given it is difficult to see, unless the fact that one has always used some other less desirable expressions than those proposed be regarded as a good reason.

Rules.

"1. Employ names such as *sodium chloride, potassium sulphate, ethyl acetate,* and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle, *e. g.*, *mercurous* and *mercuric chloride, sulphurous* and *sulphuric acid.*

"2. Term compounds of metallic and alcoholic radicles with (OH), *hydroxides* and not hydrates, *e. g.*, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, etc., should be termed sodium methoxide, ethoxide, heptyloxide, etc.

"3. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride or sulphur trioxide. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen-sodium sul-

phate, hydrogen-disodium phosphate, etc., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ*.

"4. Use names such as *methane*, *ethane*, etc., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3.(CH_2)_n.CH_3$. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane: for example, $CH_3.CH_2.CH_2.CH_3$ = propylmethane; $CH_3.CH(CH_3)_2$ = isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

"5. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, etc., denoting the di-derivatives of the form $C_nH_{2n+1}.HC:CH.C_nH_{2n+2}$ as *α*-, and those of the form $CH_2:C(C_nH_{2n+1})_2$ as *β*-compounds: thus $CH_3.CH:CH.CH_3$ = *α*-dimethylethylene; $CH_3:C(CH_3)_2$ = *β*-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH:C.C_nH_{2n+1}$ and $C_nH_{2n+1}.C:C.C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2:C:CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

"6. Distinguish all alcohols, *i. e.*, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*, *e. g.* quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol; furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5.OCH_3$, etc., hitherto called anisol, anethol, etc., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

"Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

"7. Bodies such as the acids of the lactic series containing the group (OH) should be termed *hydroxy*-, and not oxy-derivatives, *e. g.* hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3.COO$, etc., should in like manner be termed ethoxy-, phenoxy-, acetoxy-derivatives. Thus, ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyllactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2.COOH$, and not $C_6H_3(OC_2H_5)_2.COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2.COOH$.

"8. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 1).

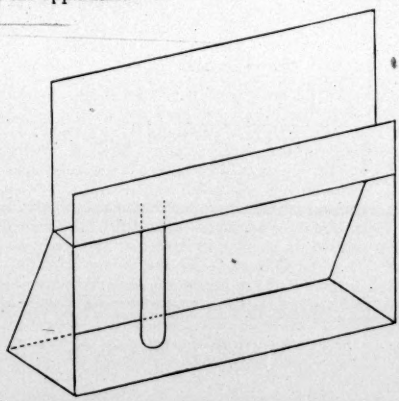
"9. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or, failing this, *sulpho-compounds:* as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2.NH_2$ should be termed sulphonamides.

"10. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz. glycerides, glucosides, bitter principles, and proteids, *e. g.* palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen, chloride, bromide or iodide, should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate."

NOTES.

Note on a Tube-Stand for Nesslerizing.

A short time since, while making some determinations by Wanklyn's method of water analysis, we were much troubled by cross-lights, which made it impossible to obtain satisfactory readings. After several attempts we hit upon the following form of stand, which has given the most excellent results, and which has the advantage of being easily and cheaply made. The following figure represents the apparatus.



The tall shield consists of a piece of quarter-inch board six inches wide tacked to the cross-piece. The low shield is three inches wide. The stand and shield are painted black. Over the bottom piece a strip of ordinary window glass, painted white on the under side, is laid. Instead of painting, which of course must be done with a pigment not affected by the laboratory fumes, a piece of white paper may be inserted between the glass and the wood, or the wood itself may be given a coat of white paint. The latter method is in some respects the most advisable, for there is then no danger of breaking the tubes by dropping on the glass. Another advantage is that the wood may receive slight hollows so as to steady the tubes and hold them perpendicular. The whole stand can also be easily made from sheet-iron.

The tubes are ordinary 7-inch test-tubes holding about 60 cc. They project about an inch and a half above the level of the perforated cross-piece. When filled the liquid is about level with the surface of the cross-piece. We find it convenient to mark the number of tenths of ammonia represented by the standard tube on the upright shield behind it. The standard tubes are placed in every other hole, the intermediate holes being used for the tubes containing the distillates. We are in the habit of using two stands each containing twenty holes and ten standard tubes, the two running from 0.01 to 0.20. The tube containing the distillate, after being treated with the Nessler solution, is placed between the two standard tubes to the color of which it approximates the most nearly, and the reading then made.

The stand is placed with the tall upright toward the light. On looking down into the tube, the color appears with remarkable clearness and brilliancy, thus rendering the reading very accurate and satisfactory.

P. T. AUSTEN AND F. A. WILBUR.

NEW BRUNSWICK, N. J.

On Silicon.

It is known that platinum heated in a forge fire, in contact with carbon, becomes fusible. Boussingault has shown that this is due to the formation of a silicide of platinum by means of the reduction of the silica of the carbon by the metal. MM. P. SCHÜTZENBERGER and A. COLSON have produced the same phenomenon by heating to white heat a slip of platinum in the centre of a thick layer of lamp-black free from silica.

The increase in weight of the metal and the augmentation of its fusibility were found to be due, in this case also, to a combination with silicon. As the silicon could not come directly from the carbon which surrounded the platinum, MM. Schützenberger and Colson have endeavored to discover under what form it could pass from the walls of the crucible through a layer of lamp-black several centimetres in thickness, in spite of a volatility amounting to almost

nothing under the conditions of the experiment. They describe the following experiments as serving to throw some light upon the question:

1. A thin slip of platinum rolled in a spiral is placed in a small crucible of retort carbon closed by a turned cover of the same material. This is placed in a second larger crucible of refractory clay, and the intervening space filled with lamp-black tightly packed. The whole is then heated to white heat for an hour and a half in a good wind furnace. After cooling the platinum is generally found to have been fused into a button with a marked increase in weight due to taking up silicon, which has penetrated in the form of vapor through the walls of the interior crucible.

2. If in the preceding experiment the lamp-black be replaced by a mixture of lamp-black and rutile in fine powder, the slip of platinum remains absolutely intact and does not change in weight. Thus the titaniferous packing recommended by Sainte-Claire Deville for preventing the access of nitrogen in experiments at high temperatures also prevents the passage of silicon. A mixture of carbon and finely divided iron is on the contrary ineffectual. These facts seem to indicate that nitrogen plays a part in the transportation of the silicon, as this is only prevented by the same means made use of in order to prevent the passage of nitrogen.

3. The volatility of free silicon at a high temperature is too slight to account for the alteration of the platinum at a distance. This can be shown by placing several decigrams of crystallized silicon on the bottom of a small crucible of retort carbon, covering the silicon with a small flat disk of retort carbon upon which is placed the slip of platinum. The crucible closed by its turned cover is then enveloped in a titaniferous packing and kept at a brilliant white heat for an hour and a half. The metal is found to have only very slightly increased in weight, and its properties remain unaltered. This experiment was repeated several times with the same result. If, however, the crystallized silicon be replaced by powdered calcined silica, the platinum, placed upon the carbon disk, fuses and increases in weight, while the silica loses weight. The theory of these curious phenomena is very difficult to establish on account of the high temperatures which are necessary for their manifestation, but it may be concluded, at present, that nitrogen and probably oxygen also play some part in the transportation of the silicon across the intervening space, and that the carbosilicious compounds recently described by MM. Schützenberger and Colson also take part in the phenomenon.—(*Comptes rendus*, **94**, 1710.) R. D. C.

On the Pretended Compound NH_5.

In a recently published article,[1] E. J. Maumené studies the action of potassium permanganate upon ammonium oxalate, by which

[1] Comptes Rendus, **94**, 571.

he professes to have obtained a new compound, to which he gives the formula NH_2. Inasmuch as the existence of a compound NH_2 or rather N_2H_4 (hydrazine) is in no way improbable from a theoretical point of view, seeing that the ethyl and phenyl derivatives of hydrazine are known, it appeared interesting to M. COMBES to repeat the experiments of M. Maumené, which he did with the following results:

1. The carbonate described by Maumené, when treated with hydrochloric acid, gives with platinum chloride a precipitate, the appearance and crystalline form of which are exactly similar to ammonium platinochloride. The analysis of the precipitate shows that it contains from 1.90 per cent. to 1.96 per cent. of hydrogen, while ammonium platinochloride contains 1.80 per cent., and the compound of Maumené only 1.35 per cent.

2. The aqueous solution of the so-called NH_2, neutralized with hydrochloric acid and evaporated to dryness, gives crystals which are absolutely identical with those of ammonium chloride; fractional crystallization always gives the same result. The analysis of this chloride gives from 7.35 per cent. to 7.52 per cent. for its content of hydrogen; ammonium chloride contains 7.47, and the chloride of NH_2 should contain only 5.71 per cent. The only products, then, of the reaction described by M. Maumené are ammonia and carbonic acid.—(*Comptes rendus*, **94**, 1717). R. D. C.

Artificial Production of Witherite, Strontianite and Calcite.

L. BOURGEOIS has found that the carbonates of barium, strontium and calcium can be easily crystallized under the ordinary pressure in a bath of certain fused materials. That which has given the best results consists of a mixture of equal equivalents of the chlorides of sodium and potassium. This mixture fuses at dark red heat, and if a few decigrams of precipitated carbonate of barium, strontium or calcium be added to the fused mass, the salt is seen to sink to the bottom of the crucible without the least effervescence. After a few minutes the fused mass is allowed to cool, and the chlorides of sodium and potassium dissolved by washing with water, when there are obtained fine crystals of carbonate of barium, strontium or calcium, identical in their chemical composition and physical properties with the natural mineral species. The carbonate of barium is generally found in hexagonal plates, which under a microscope exhibit faint polarization colors. The carbonate of strontium has only been found in the form of elongated prisms with very marked double refraction, and the carbonate of calcium constantly presents an assemblage of crystals resembling those of snow. When placed under a microscope these hexagonal stars appear colored, and if convergent light be applied they show a black cross completely surrounded by circular rings. —(*Comptes rendus*, **94**, 991.) R. D. C.

On two new Antiseptics: the Glyceroborates of Calcium and of Sodium.

G. Le Bon calls attention to two new powerful antiseptic agents, the glyceroborates of calcium and of sodium. The first is prepared by mixing equal parts of borate of calcium and glycerine, and heating the mixture to about 160° with constant stirring; the operation is prolonged until a drop of the mixture allowed to fall from the end of the stirring rod upon a glass plate solidifies on cooling to a clear colorless brittle bead. The hot liquid is then poured out upon a metallic plate and allowed to cool, when it assumes the form of a transparent mass, like glass, which is easily broken up; the fragments while still warm are rapidly introduced into a well stoppered, perfectly dry bottle. The glyceroborate of sodium is prepared in the same manner, simply replacing the borate of calcium by borate of sodium; if, however, fused or anhydrous borate of sodium be used, the proper proportions are 150 parts of glycerine to 100 parts of borax. These two compounds have analogous properties; they fuse at about 150° and are very hygroscopic; exposed to the air they rapidly become liquid, taking up their weight of water. A given quantity of water or alcohol can, however, dissolve twice its weight of glyceroborate. Even in dilute solutions the glyceroborates of calcium and sodium are very powerful antiseptic agents, and present the advantages over phenol of being readily soluble in water in all proportions, entirely without odor, and, above all, in no way poisonous. From a therapeutic point of view the sodium salt seems to be somewhat preferable to the glyceroborate of calcium. Concentrated solutions may be applied to organs as sensitive as the eye without inconvenience. The glyceroborates have also been made use of with entire success to preserve meat during a long voyage.—(*Comptes rendus*, **95**, 145.)

R. D. C.

The Luminous Incomplete Combustion of Ether and other Organic Bodies.

The author's attention was called to this subject by observing a pale blue flame floating above the hot sand of a sand-bath when evaporating some ether in the dark. He mentions that the phenomenon has previously been observed by Davy, Doebereiner, and others. Further investigation showed that ether vapor begins to burn with this blue flame at 260°. The experiment may be adapted for lecture illustration by dropping ether on an iron plate heated very nearly to redness; or better, by suspending a hot iron or copper ball over a dish containing filter papers drenched with ether. The temperature of this flame is such that the hand can be held in it with impunity. It will not char paper or ignite carbon disulphide. In large quantities it soon changes into ordinary combustion.

An experiment to determine the products of this incomplete combustion was made by aspirating air saturated with ether vapor through a combustion tube heated by a Bunsen burner, and collecting the volatile products in a test-tube surrounded by a freezing mixture, and absorbing the carbon dioxide by potash bulbs. On examining the aspirated air it was found to be nearly pure nitrogen, the oxygen being used up in the combustion, but the potash bulbs showed that only a very small quantity of carbon dioxide had been formed. For 1.313 gram of oxygen used, only 0.133 gram of carbon dioxide was formed. The products condensed in the test tube were principally aldehyde, ether, and apparently a little crotonic aldehyde. Other substances were experimented with and found to give this flame, but none so well as ether; acetic aldehyde being the next best. The alcohols up to amylic, the hydrides, and the fatty acids, except the two lower members of the series, give it with more or less distinctness. It could not be obtained from any member of the aromatic series. The products of the imcomplete combustion of paraffin were found to be similar to those of ether. The author attributes the luminous appearance to phosphorescence. The light is too feeble to be examined in detail with the spectroscope, but no bands were seen.—(W. H. PERKIN in *Journal Chemical Society*, 1882, 363). J. R. D.

The Determination of Nitric Acid in Soils by Schloesing's Method.

This subject is discussed by R. WARINGTON in two papers: the first being taken up with a description of the precautions necessary in Schloesing's method, and the second in directions for collecting samples of soils and extracting the nitrates, and in a comparison of Schloesing's with the Crum-Frankland and indigo methods. The essential condition necessary to the success of this method is the entire absence of oxygen from the retort in which the reaction takes place. This is obtained by replacing the air with a stream of pure carbon dioxide, and by boiling all the reagents, including those used in the production of the carbon dioxide, immediately before using. The operation is carried on in a small tubulated retort, the bulb of which is about 1¼ inch in diameter. This is heated in a chloride of calcium bath.

The air being entirely expelled from the apparatus by a stream of carbon dioxide, and this gas partly removed by boiling a little water in the retort, the soil extract, concentrated to a very small volume, and mixed with one cc. each of hydrochloric acid and a saturated solution of ferrous chloride, is admitted through a funnel tube, and washed in with very small quantities of hydrochloric acid. The chloride of calcium bath is kept at from 130°–140° until the contents of the retort are evaporated to dryness, and then carbon dioxide is again admitted to expel all the nitric oxide. The gas

is collected over mercury, and measured by noting the difference after absorbing the carbon dioxide by potash, and after absorbing the nitric oxide by oxygen. The oxygen should be admitted in only very small excess. The apparatus may be used continuously for several experiments. There is given a series of twelve determinations by this method of nitric oxide in a standard solution of nitre, in which the amounts varied from 5 to 0.5 mg. The quantities found varied from 96.7 to 100.8 per cent. of the quantities taken, the average being 98.4 per cent.

For the collection of samples of soils, the author prefers an iron tube about 9 inches deep and not less than 6 inches square. This is driven into the earth, and the soil filling the tube cut out. It is advisable to take several samples from successive depths, but when only one can be taken it should be from the surface in dry weather. Considerable care is necessary in drying the samples, for if this be done at a temperature of from 90° to 100°, a large proportion of the nitrates is deoxidized by the organic matter and lost, while if the temperature be too low, fermentation goes on and increases the quantity of nitrates. By a number of experiments it was found that the best plan was to place the freshly collected samples in trays in layers an inch thick, and to expose these to a heat of 55° for about 24 hours. After drying, stones and roots are removed and the soil placed in bottles.

The nitrates are extracted by percolation on a filter pump. From 200 to 500 grams of soil are placed on the filter and 100 cc. of water slowly added. The operation is complete in from 10 to 45 minutes, according to the nature of the soil. Experiment showed that second extracts contained no nitrates.

A series of determinations by the Crum-Frankland method, of the nitric oxide in soil extracts free from nitrates, to which a measured volume of a standard solution of nitre was added, seems to show that the organic matter interferes with the reaction. The results are not at all uniform, a few being too high, but the most of them too low, especially when small quantities were used. It is found that nitric oxide is not the only gas given off in the reaction. A similar, but shorter series made by Schloesing's method gives more uniform results. The determinations by the indigo method give only from 64.1 to 76.3 per cent.

The author concludes that Schloesing's method properly carried out is by far the best method for the determination of nitrates in presence of organic matter.—(*Journal Chemical Society*, 1882, 345).

J. R. D.

The Elementary Composition of Starch.

Although the text-books usually give $C_6H_{10}O_5$ or $(C_6H_{10}O_5)_4$ as the established formula of starch, the subject has by no means been positively settled. W. Nägeli[1] concluded from his study of

[1] Beiträge zur Kenntniss der Stärkegruppe. Leipzig, 1874.

the dextrins that starch has the formula $C_{36}H_{62}O_{31}$, *i. e.* $(C_6H_{10}O_5)_6 H_2O$. Later Sachsse[1] decided upon the same formula, while recently Pfeiffer and Tollens[2] have shown with some probability that it is $C_{24}H_{40}O_{20}$ or $C_{24}H_{42}O_{21}$, without being able to decide between these formulas.

Elementary analysis has not given satisfactory results, partly, at least, because of the great hygroscopicity of the anhydrous substance. Sachsse converted a weighed quantity of starch into dextrose by boiling with an acid, and determined the dextrose. If the decomposition takes place according to the equation $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$, then one part of starch should give 1.1111 parts dextrose. If, however, the reaction is expressed by $C_{36}H_{62}O_{31}+5H_2O=6C_6H_{12}O_6$, then one part starch should give 1.0909 parts dextrose. The possibility of determining the percentage composition of starch by this method depends, 1st, upon the possibility of converting all the starch into dextrose without the formation of secondary products; 2d, upon the possibility of accurately determining the dextrose thus formed. Each of these steps presents considerable difficulty. The saccharification was successfully accomplished by Sachsse, but his method of determining dextrose was faulty, and hence his conclusions were unreliable.

Salomon has attempted to solve the problem by the same method, but using for the determination of dextrose Allilin's method[3] as well as determination of the optical rotation and of the specific gravity of the solutions obtained. The values obtained in numerous experiments varied from 1.106 to 1.1131 parts dextrose from 1 part starch; whence, as shown above, the formula of starch must be $(C_6H_{10}O_5)_4$. Pfeiffer and Tollens[4] obtained a compound of the formula $C_{24}H_{39}O_{20}K$ or $C_{24}H_{41}O_{21}K$, or for starch $C_{24}H_{40}O_{20}$ or $C_{24}H_{42}O_{21}$. Analysis failed to decide between these, but showed that starch contains 24 atoms of carbon in the molecule, or a multiple of this quantity. Combining their result with that of Salomon we have as the most probable formula of starch, $C_{24}H_{40}O_{20}$.—(*Journal für praktische Chemie*, [2] **25**, 348.) H. N. S.

Tellurium Sulphur Trioxide.

A century ago Müller von Reichenstein observed that tellurium dissolves in strong sulphuric acid, imparting to it an amethyst-red color. Klaproth[5] observed that this color disappeared on dilution with water, the tellurium being precipitated. From this fact Magnus[6] concluded that the color was due to solution of free tellurium, while Fischer[7] maintained the existence of a definite com-

[1] Chemisches Centralblatt, 1877, 732.
[2] Annalen der Chemie, **210**, 294.
[3] Journal für praktische Chemie, [2] **22**, 22.
[4] Annalen der Chemie, **210**, 29.
[5] Crelle's Annalen, **1**, 98, 1798.
[6] Poggendorff's Annalen, **10**, 492; **14**, 328.
[7] Poggendorff's Annalen, **12**, 153.

pound, calling attention to the difference of color between tellurium and its solution, and to the fact that on dilution with water some of it remains in solution as oxide. The question has since been occasionally discussed, but without result. Similar phenomena were observed when sulphur and selenium are dissolved in fuming sulphuric acid, the former giving a blue, the latter a green color. RUDOLPH WEBER[1] obtained bodies of the composition S_2O_3 and $SeSO_3$, by the action of sulphur and selenium on sulphur trioxide, and showed that the blue and green color of the acid is due to solution of these bodies. He now describes an analogous compound $TeSO_3$, which is thus prepared: Finely powdered and carefully dried tellurium is brought in small portions into perfectly anhydrous sulphur trioxide, which is kept at the temperature of 30°–35°. The tellurium changes at once into a red viscous mass, while the trioxide, if pure, remains colorless. The excess of trioxide is then poured off, and that still adhering very carefully evaporated. Thus obtained, the substance is a red amorphous mass, viscous at ordinary temperatures, and transparent only in thin layers, when it shows the amethyst-red color. It soon decomposes at common temperatures, even in close vessels, becoming black with precipitated tellurium and evolving sulphur dioxide. When warmed it is decomposed into Te, TeO_2, SO_2 and some SO_3. It is also instantly decomposed by water, yielding the same products. It is insoluble in perfectly anhydrous sulphur trioxide, but dissolves in common or fuming sulphuric acid, with amethyst-red color. The mean of six analyses gave Te 61.13 per cent. (from 60.40 to 61.81 per cent.) Calculated for $TeSO_3$, Te 61.54 per cent. It is hence analogous to S_2O_3 and $SeSO_3$, which it resembles in chemical and physical properties.—(*Journal für praktische Chemie*, [2] **25**, 218.) H. N. S.

Preparation of Mustard Oils.

A. W. HOFMANN states that the mustard oils are best prepared from the disubstituted sulpho-ureas by treating them with a concentrated aqueous solution of phosphoric acid. The sulpho-ureas are easily obtained by treating carbon bisulphide with the amines. Starting with carbon bisulphide and aniline we get diphenyl-sulphourea, $CS(C_6H_5)H_2N$; and when this is treated with phosphoric acid it breaks up directly into aniline and phenyl-mustard oil, thus:

$$CS(C_6H_5)_2H_2N_2 = C_6H_5(NH_2) + \underset{\text{Mustard Oil.}}{C_6H_5NCS},$$

—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 985.)

[1] Poggendorff's Annalen, **156**, 531.

Preparation and Basicity of Hyponitrous Acid.

Hyponitrous acid has hitherto been obtained by treating a nitrate or nitrite with sodium amalgam, or by the electrolysis of sodium nitrate or nitrite, mercury being used as the negative electrode. W. ZORN now finds that it may be readily obtained by treating sodium nitrite with ferrous hydroxide. Milk of lime is added to ferrous sulphate, and to the mixture of ferrous hydroxide and gypsum thus formed is added a solution of sodium nitrite (1 part nitrite to 10 parts ferrous sulphate). The reaction is complete in a few hours. The mass is strained and pressed, and then carefully neutralized with acetic acid. On adding silver nitrate, a precipitate of pure silver hyponitrite (commonly called nitrosyl silver) is formed. The author asserts that Menke's statement that sodium hyponitrite is formed by fusing sodium nitrate with iron filings is not correct, and that Menke must have had either carbonate or phosphate of sodium. When silver hyponitrite is treated with ethyl iodide, a substance of the formula $C_2H_5-N_2O_2-C_2H_5$ is formed. This appears to be an ester of hyponitrous acid, although its reactions indicate that it is a diazo-compound. An acid barium salt was obtained, corresponding to the formula $Ba(O_2N_2)N_2O_2H_2$, the existence of which shows that hyponitrous acid is bibasic and has the formula $N_2O_2H_2$.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1007 and 1258.)

On the Oxidation of Symmetrical Nitroxylene.

The researches of Remsen and his co-workers have shown that when an aromatic hydrocarbon which contains two hydrocarbon residues and a negative substituting atom or group is subjected to the action of chromic acid, that residue which is in the para or meta position is oxidized, whereas the residue in the ortho position is protected. E. WROBLEWSKY has now shown that when symmetrical nitroxylene, that is, the one in which each group is in the meta position with reference to both the others, is oxidized, both methyl groups are converted into carboxyl.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1021.)

The Dismemberment of Tropine.

A. LADENBURG in a third communication on this subject shows that tropilene is converted by nitric acid into an acid of the formula of adipic acid, $C_6H_{10}O_4$, and probably identical with this. He has further found that, when tropidine is treated with bromine in sealed tubes, it is converted into dibrom-methylpyridine, ethylene bromide being formed at the same time. The reaction may be represented thus:

$$C_7H_{11}N + 4Br_2 = C_2H_4Br_2 + C_6H_5Br_2N + 4HBr.$$

This makes it appear probable that tropidine is a hydrogen addition product, and ethylene derivative of methylpyridine of the formula $C_5H_6(C_2H_4)NCH_3$. For tropine he suggests the formula $C_5H_7(C_2H_4(OH))NCH_3$.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1028.)

Conversion of Pyrrol into Pyridine.

G. L. CIAMICIAN and M. DENNSTEDT have succeeded in obtaining monobrompyridine from pyrrol by the following method: Pyrrol potassium, C_4H_4NK, was treated with bromoform, when action took place, thus:

$$2C_4H_4NK + CHBr_3 = C_4H_4NH + C_5H_4BrN + 2HBr.$$

A careful comparison of the product with that obtained by the action of bromine on pyridine proved the identity of the two.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1172.)

Action of Hydrogen Peroxide on Organic Matters and Fermentations,—On the Employment of Hydrogen Peroxide in Surgery.

MM. PAUL BERT and P. REGNARD have studied the action of hydrogen peroxide upon various forms of organic matter and upon fermentations, and find that it possesses very remarkable antiseptic properties. All fermentation due to an organized ferment is immediately and definitely arrested by hydrogen peroxide, the ferment is killed, and even after the removal of the hydrogen peroxide by one of the substances which destroys it most rapidly, the fermentation does not recommence. The yeast of beer is in this manner killed instantly, although it possesses itself the property of decomposing hydrogen peroxide. Specimens of wine, urine, and milk, each containing a few drops of hydrogen peroxide, have been exposed for several months in open vessels without exhibiting the least sign of alteration, while other specimens of the same identical liquids, without the addition of hydrogen peroxide, placed beside them, were in a state of complete decomposition. Although organized ferments are destroyed by hydrogen peroxide, soluble ferments do not seem to be affected by it, saliva, diastase, the gastric and pancreatic fluids continue to act in solutions containing hydrogen peroxide. MM. Bert and Regnard have also studied the action of hydrogen peroxide upon various organic materials, including the albuminoid substances, and all the tissues composing the animal body in a healthy or pathological state. The results of their investigations may be summed up as follows:

1. Hydrogen peroxide, even when very dilute, arrests fermentations due to the development of living organisms, and the putrefaction of all substances which do not decompose it.

2. It has no effect upon diastase fermentations.

3. Dilute hydrogen peroxide is not destroyed by fats, starches, soluble ferments, egg albumen, casein, the peptones, creatine, creatinine or urea.

4. It is rapidly destroyed by nitrogenous collagens, by musculin, fibrin of the blood, and various nitrogenous vegetable matters.

5. This action is definitely arrested by a temperature above 70°. Putrefaction, however, leaves it entirely intact.

As it appeared from the powerful antiseptic properties of hydrogen peroxide that it might prove of value in surgery, experiments were made upon the point by MM. PÉAN and BALDY at the hospital of St. Louis, with very successful results.

The hydrogen peroxide, in solutions containing from two to six times its volume of oxygen, according to the circumstances of the case, was used, both externally, as a dressing for wounds, ulcers, etc., and also given internally in certain affections, in doses of from three to five grains, containing six times its volume of oxygen. As a result of their experiments MM. Péan and Baldy consider themselves justified in stating:

1. Hydrogen peroxide containing, according to circumstances, from two to six times its volume of oxygen, appears to be capable of advantageously replacing alcohol and carbolic acid.

2. It can be employed, externally, for the dressing of wounds and ulcerations of all natures, in injections and in vaporizations, and internally,

3. The results obtained, even in the case of the largest operations, are, up to the present, in the highest degree satisfactory. Not only fresh wounds, but also old ones, proceed rapidly to cicatrization, and reunion by first intention of amputation wounds appears to be encouraged by this mode of dressing.

4. The general as well as the local state appears to be favorably influenced.

5. The advantages of hydrogen peroxide over carbolized water are its not having any poisonous effect nor unpleasant odor, while its application is entirely painless.

M. Bert calls attention to the fact that hydrogen peroxide for surgical use must be entirely neutral, while that obtained from the greater number of dealers in chemicals frequently contains a considerable quantity of sulphuric acid, so that its use would not be without danger.—(*Comptes rendus*, **94**, 1383, *and* 95, 49.)

R. D. C.

Disinfectants.

In an article[1] on disinfection Dr. R. Koch remarks that the only substances worthy of the name of disinfectants are chlorine, bromine, iodine, mercuric chloride, and perhaps potassium perman-

[1] Mittheilungen des kaiserlichen Gesundheitsamtes **1**, 1881.

ganate and osmic acid. He finds that spores of the bacillus of splenic fever, kept for many days in 5 per cent. zinc chloride solution, develop when placed in suitable nutritive liquids, even when added to serum containing ½ per cent. zinc chloride. He wonders how this salt could ever have been regarded as an antiseptic.

FR. BOILLAT, in criticising Koch's article, calls attention to the fact that for a substance to be an antiseptic it is not necessary for it actually to *destroy* germs. In the antiseptic treatment of wounds it would be impossible to employ such violently acting substances as those mentioned by Koch. All that is necessary is the presence of substances capable in some way of restraining the development of germs, which hence may properly be called antiseptics. Many antiseptics have the power of coagulating proteids. Boillat prepared such coagula from serum and egg albumin by precipitating with phenol, zinc chloride, copper sulphate and mercuric chloride. These albuminates, after being well washed to remove any excess of the precipitant, were mixed with a little water and exposed to the air. Pure serum and Koch's gelatine served to control the experiments. In the serum, gelatine and phenol-albuminate, bacteria appeared in 1, 1 and 2 days respectively, and marked putrefaction in 2, 4 and 6 days respectively, while in the metal-albuminates bacteria did not appear until from 31 to 45 days, and marked putrefaction in from 46 to 60 days. The surprisingly rapid putrefaction of the phenol-albuminate was explained when it was found on examination to contain no phenol. Splenic fever spores were found to develop in gelatine in 1 day, and not at all in metal-albuminates. According to Boillat, Koch did not add enough zinc chloride to his serum to convert all the proteids into the harmless but innutritious zinc-albuminate, and the spores availed themselves of the excess. Applied to the surface of a wound, zinc chloride forms a superficial coating of the neutral zinc-albuminate, which affords no means for the bacteria to develop, and protects the parts under it.

Experiments with iodoform (2 per cent. sol.); carbon tetrachloride, CCl_4; the chlorides C_3Cl_4 and C_3Cl_6, and bromo-toluene (liquid and solid), and dimethyl-pyrogallol (1 per cent. sol. each), as restraining putrefaction of pancreas, gave negative results, and paracresol was active only in solutions of at least ½ per cent., and even then did not restrain the action of the pancreatic ferment. —(*Journal für praktische Chemie*, [2], **25**, 300.) H. N. S.

On the Stannous Nitrates.

At the Royal Powder Works at Spandau, Prussia, frequent ignition of the powder at a certain stage of the process led to an examination of the machinery, when it was found that where at certain parts bronze pieces which were soldered were in constant contact with

the moist powder, the solder was much corroded and in part entirely destroyed, and that in the joints had collected a substance which on being scraped out with a chisel, exploded with emission of sparks. It was suspected that the formation of this explosive material was in some way connected with the corrosion of the solder, and the subject was referred for investigation to RUDOLPH WEBER, of the School of Technology at Berlin. The main results of his investigation are here given.

The explosive properties of the substance indicated a probable nitro-compound of one of the solder metals (tin and lead), and as the lead salts are more stable and better understood than those of tin, it was resolved to investigate the latter, in hope of obtaining a similar explosive compound. Experiments on the action of moist potassium nitrate on pure tin led to no result, as no explosive body was formed. Stannous nitrate, $Sn(NO_3)_2$, formed by the action of dilute nitric acid on tin, has long been known, but only in solution, as it is decomposed on evaporating. By adding freshly precipitated moist brown stannous oxide to cool nitric acid of sp. gr. 1.20, as long as solution occurred, and then cooling the solution to —20°, Weber obtained an abundance of crystals of the composition $Sn(NO_3)_2 + 2OH_2O$. They resemble crystals of potassium chlorate. They cannot be kept, as they liquefy at ordinary temperatures. An insoluble *basic* salt was obtained by digesting an excess of moist stannous oxide in solution of stannous nitrate, or by adding to a solution of stannous nitrate by degrees, with constant stirring, a quantity of sodium carbonate solution insufficient for complete precipitation. Thus obtained, the basic salt, which has the composition $Sn_2N_2O_7$, is a snow-white crystalline powder, which is partially decomposed by water, and slowly oxidized by long exposure to the air or by heating to 100°. By rapid heating to a higher temperature, as well as by percussion and friction, it explodes violently, giving off a shower of sparks. This compound is also formed when a fine spray of nitric acid (sp. gr. 1.20) is thrown upon a surface of tin or solder. It is also formed when tin or solder is exposed to the action of a solution of copper nitrate, and thus formed presents the properties already described.

In this, then, we have a probable cause of the explosions occurring in the powder works; but the explanation of the formation of the substance is wanting, as potassium nitrate was shown not to give an explosive substance with tin. A thin layer of a mixture of sulphur and potassium nitrate was placed between sheets of tin and copper foil, and allowed to stand, being kept constantly moist. After a time the copper was found to have become coated with sulphide, while the tin was largely converted into the explosive basic nitrate. The conditions are obviously the same as those found in the powder machinery, where bronze and tin solder are constantly in contact with moist gunpowder. The chemical action is probably this: the sulphur of the powder forms with the copper of the bronze, copper sulphide; this is oxidized to sulphate, which

reacts with the nitre of the powder, forming potassium sulphate and copper nitrate; the latter, as shown above, then forms with the tin of the solder the explosive basic nitrate, which, being insoluble, gradually collects in the joints and finally leads to an explosion.—(*Journal für praktische Chemie*, [2], **26**, 121.)

H. N. S.

The Earth-Metals in Samarskite.

H. E. Roscoe has studied the group of rare earth-metals found in samarskite with a view to the separation of philippium. The coarsely powdered mineral was treated with hydrofluoric acid, which gave a greenish precipitate. This, after drying, was dissolved in sulphuric acid, and, after removing uranium by nitric acid, the earth-metals were precipitated by ammonium oxalate. The oxalates were converted by ignition into oxides, and these into nitrates, which were fused, dissolved in water, and from this solution the metals were separated into two groups by fractional precipitations from a solution of potassium sulphate. The more soluble of these two groups, containing the yttrium, philippium and terbium, after conversion of the sulphates into oxides, was treated with formic acid, and submitted to a long series of fractional precipitations. It was found impossible to obtain in this way the formate of a metal having a constant weight between 121 and 123, but the formate agreeing most closely with these numbers possessed distinct physical properties, differing very decidedly from those obtained from higher or lower fractions. In order to determine if this salt was a double formate of other metals, a mixture of two solutions of the formates of yttrium and terbium was made, and from this rhombic crystals were obtained with properties exactly like those attributed to philippium.—(*Journal of (London) Chemical Society* **41** (1882), 277.) J. R. D.

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